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SUPPLEMENT TO MELLOR'S COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

VOLUME VIII
SUPPLEMENT II
N (Part II)

A COMPREHENSIVE TREATISE ON
INORGANIC AND THEORETICAL CHEMISTRY

By J. W. Mellor, D.Sc., F.R.S.

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	Supp. II.	N (Part II).

Literature Abbreviations to Vol. VIII
Supps. I and II

QP
31
.M52
vol. 8
Suppl. 2

Supplement to

MELLOR'S COMPREHENSIVE
TREATISE ON

INORGANIC
AND THEORETICAL
CHEMISTRY

Prepared under the direction
of an Editorial Board

VOLUME VIII
SUPPLEMENT II
Nitrogen (Part II)

1724

LONGMANS

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First published 1967

Made and printed in Great Britain by
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PREFACE

In the first supplementary volume on Nitrogen consideration was confined to the production and properties of elementary nitrogen, ammonia and certain common ammonium salts, and the biological activity of nitrogen and its compounds in general. In the present Supplement other compounds of nitrogen and hydrogen, the oxides, oxy-acids and halides of nitrogen, the isotopy, spectroscopy and radiation chemistry of nitrogen, and the analytical chemistry of the element and its compounds are reviewed. In accordance with Dr. Mellor's convention the nitrates are treated under the appropriate metals (or ammonium) but the salts of other nitrogen oxy-acids are considered here. This division of the Nitrogen Supplement did not arise from any fundamental distinction, but was conditioned partly by the varying time schedules of the completion of the relevant sections and partly by a desire to present for the use of chemists and chemical technologists without undue delay those sections which were already complete and could reasonably be linked in the same volume.

The procedure so successfully employed in the preparation of earlier Supplements has been extended unchanged to the present volume of the series. Specialist contributors, provided with information derived mainly from *Chemical Abstracts*, and encouraged freely to make use of the corresponding original papers and any other sources of published information, have written their accounts of the various aspects of the chemistry of nitrogen with minimal detailed editorial direction, so that the breadth and depth of treatment in a section will largely reflect the judgment of its author. Two desiderata have, however, been specially borne in mind: first that the Treatise should not be merely a collection of 'signposts to knowledge', but should freely present precise facts and quantitative data, frequently in tabulated form, and second that as far as possible the original source of every statement and its *Chemical Abstracts* reference should be quoted. In this way it is hoped to contrive that the chemist can not only quickly obtain a reasonably complete picture of useful up-to-date information or criticism in the fields of his interest, but also be clearly directed either to such further details as may be quoted by *Chemical Abstracts* or, if need be, to the original paper itself. In the preface to Volume II Supplement I (originally termed Supplement II Part I) the considerations on which the editors based their policy and the technique which they adopted were stated in some detail. Neither policy nor technique has needed alteration; indeed the editors are by their experience confirmed in their view that for the compilation of a work having such breadth of horizon and complexity of structural content the method adopted is the only one which, in this era of vast expansion of chemical investigations and seemingly contraction of the time available for their digestion, has practical merit. While necessarily excluding matter judged to be irrelevant or of relatively small importance, the editors and contributors have steadfastly borne in mind the significance of the description 'Comprehensive' in the title of the work, interpreting it the more rigidly in the domain of inorganic and physical chemistry, and correspondingly less rigidly in other fields, particularly in those of organic chemistry and cognate fields of study which, though falling beyond the boundaries of the main purpose of the work, nevertheless provide some of its background material.

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ACKNOWLEDGEMENTS

In the preparation of these Supplements the Editors and Contributors have endeavoured to ensure that the source of every observation or comment to which reference is made should be not only acknowledged, but also indicated with such precision and clarity that it can quickly be traced and studied by a reader to whom the necessary library facilities are available. In their study of original papers the Contributors have made use of libraries of various University institutions and Colleges of Technology, of the Science Library, of the Patent Office library and of the libraries and reference indexes of certain industrial firms. Acknowledgements should therefore be made here of the participation of many intermediaries in this process of compilation; the Editors would wish to emphasize their indebtedness to all those who have played an essential part in the collection, abstraction, indexing and preservation of the material forming the original subject matter brought to the attention of Contributors by way of the relevant abstracts published by the American Chemical Society in *Chemical Abstracts* and discussed in this volume.

In particular the warm thanks of the Editors are offered to Imperial Chemical Industries Ltd. (Agricultural Division), to Messrs Whiffen and Sons Ltd. and to Messrs Fisons Ltd. for their encouragement and for providing valuable facilities for the study by nominated contributors of published information in their fields of activity and interest. No less warmly do the Editors acknowledge the help they have received from Dr. A. G. Maddock who made material suggestions concerning, inter alia, the treatment of the radiation chemistry of nitrogen, and from Professor G. R. Martin who with Dr. Maddock advised on the section in which the isotopes of nitrogen are discussed. By undertaking at very short notice the preparation of the section on the analytical chemistry of nitrogen and its compounds, and by his energetic execution of this task, Dr. K. I. Vasu has contributed significantly to the limitation of delay in the publication of this Supplement. This delay has necessarily precluded detailed discussion of some very recently developed aspects of the chemistry of nitrogen.

As always, Messrs Longmans, Green and Co. Ltd. have given the Editors much sound advice and technical assistance and individual members of the Company's staff have once again been most ready to place noteworthy expertise at their disposal.

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Once again permission to use information tabulated in *Table of Isotopes* by Strominger, Hollander and Seaborg has contributed notably to the usefulness of the section on Isotopes. The table from *The Threshold of Space* by M. Zelikoff is reproduced by permission of Pergamon Press Ltd.

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ABBREVIATIONS

absolute	abs.
alternating current	a.c.
ampère-s	amp.
Angstrom unit-s	A.
atmosphere-s (after a numeral)	atm.
atomic weight	at. wt.
boiling point	b.p.
British thermal unit-s	B.Th.U.
Calorie-s (large)	kcal.
calorie-s (small)	g.-cal.
centimetre-s	cm.
cubic centimetre-s	c.c.
density (with a numeral)	ρ, d
direct current	d.c.
electromotive force	e.m.f.
foot, feet	ft.
freezing point	f.p.
gram-s (with a numeral)	g.
hour-s (with a numeral)	hr.
inch-es	in.
kilogram-s	kg.
kilowatt-s	kw.
litre-s (with a numeral)	l.
melting point	m.p.
milliampère-s	ma.
millilitre-s	ml.
millivolt-s	mv.
minute-s	min.
molecular weight	mol. wt.
parts per million	p.p.m.
potential difference	p.d.
second-s (time only)	sec.
specific gravity	sp. gr.
square centimetre-s	sq. cm.
vapour density	v.d.
vapour pressure	v.p.
volt-s	v.
watt-s	w.
wave-length	λ

Abbreviations of Journal titles, etc., in references are listed in Volume VIII, Supplement 1, Nitrogen (Part I), pp. xi–lxviii; they are also published as a separate booklet available through any bookseller who supplies the Mellor Supplements. A few additional abbreviations have unavoidably been introduced; these conform to current practice in "Chemical Abstracts".

NITROGEN

SECTION XVIII

HYDROGEN AZIDE

BY K. G. MASON

Formation

THE formation of hydrogen azide during the Raschig synthesis of hydrazine was attributed by F. Sommer (Mellor, VIII, 332) to the oxidation of the hydrazine by nitrous acid; later workers also subscribe to this explanation.[1] The hydrogen azide liberated by the action of sulphuric acid on sodium azide can be removed easily and safely by distillation under reduced pressure.[2] The action of sulphuric acid on barium azide affords pure aqueous hydrogen azide.[2]

Gaseous hydrogen azide can be prepared by the action of molten stearic acid on sodium azide; since the reaction occurs only with the molten acid it is easily controlled.[3] The action of syrupy phosphoric acid on sodium azide also affords a convenient mode of preparation of gaseous hydrogen azide.[4, 5]

The direct synthesis of hydrogen azide by a glow discharge method has been described.[6]

Physical Properties

The vapour pressure of pure hydrogen azide (p mm.) has been represented by the relation[70]:

$$\log_{10} p = 8{\cdot}198 - \frac{1643}{T}$$

The vapour pressure curve, from near the triple point to near the boiling point, has been constructed and by extrapolation the boiling point was estimated to be 35·7°.[3] The molecular weight of hydrogen azide was found, by pressure methods, to be 43·6 ± 2·1.[60]

The density of liquid hydrogen azide between 0° and 21°C. has been expressed by the relation[3]:

$$d_t = \frac{1{\cdot}126}{1+0{\cdot}0013t}$$

By calorimetric measurement of the heat of explosion, the heat of formation of gaseous hydrogen azide, at constant volume, was found to be $-70{\cdot}9 \pm 0{\cdot}5$ kcal./mole.[3] The heat of solution of the gas in water was determined as 9·7 ± 0·1 kcal./mole; and the heat of vaporization at 12·4° as 7·3 ± 0·1 kcal./mole.[3] Indirect calculations gave the minimum heat of decomposition of liquid hydrogen azide as 67 kcal./mole, ±5%. Calculations from Berthelot's data for dilute aqueous solutions gave approximately 53 kcal./mole.[7] The energy of activation of the decomposition of hydrogen azide was calculated to be 695 g cal./mole.[62]

The experimental determination of enthalpy data for liquid and gaseous hydrogen azide, and for the azide ion, has been described.[8, 9] The standard enthalpy of formation of hydrogen azide in water (2000 moles) was found to be 61,430 g cal./mole.[8]

The optical absorption of gaseous hydrogen azide, in the range 2000–2800 A., showed a maximum at about 2·5 cm. Hg.[10] Over the range 1–4 cm. Hg the absorption was found to be in accord with the relation:

$$\frac{I}{I_0} = K_1 - 0{\cdot}56[\mathrm{HN_3}] + 0{\cdot}11[\mathrm{HN_3}]^2$$

where K_1 varies from 0·48 at 2000 A. to 1·25 at 2400 A. and 1·11 at 2600 A. The molecular coefficients of absorption over the range of concentration 0·5 N. to 0·0002 N., between 2000 A. and 2800 A., have also been tabulated.

Chemical Properties

FORMATION OF AZIDES

Hydrogen azide is a weak acid which gives rise to a series of salts, azides, by several types of reaction. Thus aqueous hydrogen azide gives azides with metal hydroxides, oxides and carbonates, e.g. gaseous hydrogen azide is absorbed by aqueous barium hydroxide giving rise to barium azide.[11] However, in its reactions with zinc, iron, manganese, nickel and copper, hydrogen azide resembles nitric acid,[12] e.g.:

$$\mathrm{Zn + 3HN_3 \rightarrow Zn(N_3)_2 + NH_3 + N_2}\ (+\ \text{traces of } \mathrm{N_2H_4})$$

Also, a mixture of hydrogen azide and hydrochloric acid dissolves gold and platinum (cf. *aqua regia*).

Aluminium azide can be prepared almost quantitatively by adding excess of hydrogen azide, in ether, to a frozen ether solution of aluminium hydride and allowing the mixture to thaw. As the temperature rises above −116°, hydrogen is evolved and a white precipitate separates after several minutes; the ether and excess of hydrogen azide are then removed by distillation.[13] In a similar manner the reaction between hydrogen azide and lithium tetrahydroaluminate, in ether, affords lithium tetraazidoaluminate.[14] A variety of simple and mixed metal hydrides also undergo this reaction, the products from which are stable at the ambient temperature in the absence of air and moisture, but are very explosive on shock:

$$\mathrm{Al[BH_4]_3 \rightarrow Al[B(N_3)_4]_3}$$

This product contains almost 90% by weight of nitrogen.

ACTION OF NITROUS ACID

Nitrous acid reacts quantitatively with hydrogen azide thus:

$$\mathrm{HNO_2 + HN_3 \rightarrow H_2O + N_2O + N_2}$$

The advantages of this reaction for the detection of nitrous acid in the presence of large amounts of nitric acid have been stressed.[15, 16] The formation of the unstable suboxide, N_4O, which was considered to be N_2:N.NO, was suggested as the first step, instantaneous decomposition of the suboxide affording N_2 and N_2O.[15] The reaction has been studied with the aid of ^{15}N.[17] Labelled nitrite was caused to react with ordinary azide and ordinary nitrite was caused to react with labelled azide:

$$\mathrm{H}\underset{a}{\mathrm{N}}\underset{b}{\mathrm{N}}\underset{a}{\mathrm{N}} + \mathrm{H}\underset{c}{\mathrm{N}}\mathrm{O_2} \rightarrow \underset{1}{\mathrm{N}}\underset{2}{\mathrm{N}}\mathrm{O} + \underset{3}{\mathrm{N}}\underset{3}{\mathrm{N}} + \mathrm{H_2O}$$

It was found that atom *c* appeared quantitatively as atom 2 in the nitrous oxide and that one of the atoms *a* takes the place of the atom 1. The remaining nitrogen atoms *a* and *b* afforded the elementary nitrogen. The kinetics of the reaction between nitrous acid and hydrogen azide, in the presence of nitrate or halide ion, or acetate ion and acetic acid, have been studied.[18] The rate was found to be given by the expression:

$$\frac{-\mathrm{d}[\mathrm{NO_2}^-]}{\mathrm{d}t} = (k_1[\mathrm{N_3}^-] + k_2[x^-])[\mathrm{NO_2}^-][\mathrm{H}^+]^2$$

where x^- is nitrate or halide ion. The rapid formation of $NOOH_2^+$ is followed by the rate-determining decomposition by either azide or x^- ion.

The nitrite–azide reaction has been believed to be specific for trivalent nitrogen even in strong acid; it has also been found that pentavalent nitrogen reacts with hydrogen azide in concentrated acid.[19] Sodium azide was added to strongly acidified sodium nitrate and the reaction followed polarographically. The gaseous product, analysed by gas chromatography, was found to be a mixture of nitrogen and nitrous oxide with, in some cases, nitric oxide:

$$\text{(1)}\quad HN_3 + NO_2^+ \xrightarrow{k_1} 2NO + N_2 + H^+$$

$$\text{(2)}\quad 2NO + NO_2^+ + 2H^+ \xrightarrow{k_2} 3NO^+ + H_2O$$

$$\text{(3)}\quad 3(NO^+ + HN_3 \xrightarrow{k_3} N_2O + N_2 + H^+)$$

$$\text{(4)}\quad 4HN_3 + 2NO_2^+ \rightarrow 4N_2 + 3N_2O + H_2O + 2H^+$$

Reaction (3) is the nitrite–azide reaction and is very rapid even at low $[H^+]$. At concentrations less than 13 M. reaction (1) is the rate-determining one; at higher concentrations $k_1 > k_2$ and the situation is complicated.

ACTION OF SULPHURIC ACID

The action of sulphuric acid on hydrogen azide under a variety of conditions has been investigated.[20, 21] If hydrogen azide is gently heated to 100° with concentrated sulphuric acid the major product is hydroxylamine, but not in sufficient amount to agree with the equation:

$$HN_3 + H_2O \rightarrow N_2 + NH_2OH$$

The formation of sulphur dioxide indicates the occurrence of oxidative side reactions by the sulphuric acid. If a benzene solution of hydrogen azide is treated with concentrated sulphuric acid at room temperature, gas evolution takes place at the interface for several days and a large amount of hydrazine sulphate separates; the remaining solution contains a small amount of aniline and hydroxylamine. If the benzene solution and sulphuric acid are stirred at 60°C., the major product is aniline sulphate together with a little hydrazine sulphate. These observations have been explained in terms of the imine radical, NH, which is assumed to be formed by elimination of a molecule of nitrogen from the hydrogen azide. The following equations are proposed to account for the above reactions:

$$:NH + H_2O \rightarrow NH_2OH$$
$$:NH + C_6H_6 \rightarrow C_6H_5.NH_2$$
$$2:NH \rightleftharpoons N_2H_2$$
$$2N_2H_2 \rightarrow N_2 + N_2H_4$$

Further observations showed that the amount of hydroxylamine produced was one-seventh of that demanded by the equation and it was assumed that the greater part of the imine radical was oxidized by the sulphuric acid to nitrogen.[21]

Dilute sulphuric acid or gaseous hydrogen chloride acts on hydrogen azide in a different manner from that of concentrated sulphuric acid.[21] The reaction:

$$3HN_3 + HCl \rightarrow NH_4Cl + 4N_2$$

proceeds at a low rate. In the absence of other acids hydrogen azide itself takes the part of the hydrogen chloride in the above equation, and if a solution of hydrogen azide in benzene is heated, decomposition occurs in accordance with the equation:

$$4HN_3 \rightarrow NH_4N_3 + 4N_2$$

This reaction is, however, very slow and prolonged heating at elevated temperatures, e.g. 48 hours at 230°, is needed for appreciable conversion.

The above, and other, reactions of the imino radical have been reviewed.[22]

ACTION OF NITRIC ACID AND POTASSIUM PERMANGANATE

The action of dilute, concentrated and fuming nitric acid on hydrogen azide has been studied.[23] With the dilute acid no reaction at all is observed; with the concentrated acid the chief product is nitrogen together with varying amounts of N_2O, NO, N_2O_3 and NO_2. The principal reaction is assumed to be:

$$HN_3 + HNO_3 \rightarrow N_2 + 2NO + H_2O$$

Further reactions between the nitric oxide and the excess of nitric acid are assumed to be responsible for the formation of the other oxides of nitrogen. A more energetic reaction occurs between hydrogen azide and fuming nitric acid; the sole products are nitrogen and nitrous oxide.

The use of ^{15}N enables the central atom in the azide to be distinguished from the end atoms but does not enable these to be differentiated.[17, 24] Oxidation of hydrogen azide with acidic potassium permanganate affords mostly nitrogen and nitric acid together with an oxide of approximate empirical formula N_2O.[24]

REDUCTION

The catalytic decomposition of hydrogen azide by platinum black has been further studied and the following equations proposed[25]:

$$HN_3 + H_2 \rightarrow NH_3 + N_2$$
$$2HN_3 + O \rightarrow 3N_2 + H_2O$$

As an extension of a survey of the reduction of hydrogen azide the latter was reduced, in the presence of colloidal palladium, by nascent and molecular hydrogen.[26] In each case the reduction proceeds chiefly in accordance with the equation:

$$HN_3 + 6H \rightarrow NH_3 + N_2H_4$$

If the reaction medium is alkaline instead of acidic, no appreciable reduction occurs.

Raney nickel vigorously decomposes aqueous solutions of hydrogen azide and its salts.[27] It was concluded that the catalyst acts as a true reducing agent and that the decomposition is represented by the equation:

$$3HN_3 \rightarrow NH_3 + 4N_2$$

Acidic reduction of hydrogen azide with hydriodic acid or stannous chloride affords nitrogen and ammonium salts; alkaline reduction with aluminium affords hydrazine as the sole product.[24]

MISCELLANEOUS REACTANTS

Azidocarbon disulphide, which is produced by the oxidation of azidodithiocarbonic acid, reacts with hydrogen azide in ether solution[28]:

$$(SCSN_3)_2 + 8HN_3 \rightarrow 2NH_4SCN + 2S + 13N_2$$

Three principal stages are proposed for this reaction, namely:

$$(SCSN_3)_2 \rightarrow (SCN)_2 + 2S + 2N_2$$
$$(SCN)_2 + 2HN_3 \rightarrow 2HSCN + 3N_2$$
$$HSCN + 3HN_3 \rightarrow NH_4SCN + 4N_2$$

The reaction of hydrogen azide with free thiocyanogen in ether was found to be:

$$(SCN)_2 + 8HN_3 \rightarrow 2NH_4SCN + 11N_2$$

The catalytic action of thiosulphate on the reaction between iodine and hydrogen azide was explained by Raschig (Mellor, VIII, 337) on the assumption that the compound, $NaIS_2O_3$, was formed as an intermediate. A sequence of nine reactions has been proposed in an attempt to account for the catalysis without the formation of the above intermediate.[29] The same sequence was applied to the nitrous acid catalysed reaction, whereas a sequence of eight reactions was suggested for the uncatalysed reaction between hydrogen azide and iodine. Reaction sequences have also been proposed to account for the catalysis of this reaction by tetrathionates[30] and thiocyanates.[31]

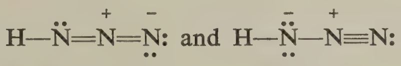
Hydrogen azide, like the hydrogen halides, forms a sparingly soluble salt with strychnine, and gives typical crystals when treated with a solution of mercuric acetate and hexamethylenetetramine.[32]

The reaction between hydrogen azide and sulphur chloride, S_2Cl_2, has been studied.[33]

The colour reaction between hydrogen azide and ferric ions has been investigated in some detail.[34]

The Structure of Hydrogen Azide

Although a considerable amount of evidence had accumulated which indicated that the nitrogen atoms in hydrogen azide are linear, some authors still advocated the cyclic structure.[35, 36] Indeed, in a critical survey of the literature, the conclusions reached were that qualitative experimental evidence based mainly on the behaviour of hydrogen azide inorganic syntheses favours a cyclic structure and that physico-chemical studies indicate the linear form.[37] However, further investigations demonstrated quite clearly that the nitrogen atoms are linear. Thus, in the photographic infra-red region, the rotation–vibration spectrum of hydrogen azide gas was found to have an intense band at $1{\cdot}045\ \mu$ and a weaker one at $0{\cdot}808\ \mu$.[38] The fine structure of these bands indicated that the three nitrogen atoms are almost linear, and that the hydrogen atom does not lie on the same line in the majority of the molecules. The application of Pauling's adjacent-charge rule and the values of the appropriate moments of inertia also support the linear structure.[39] Electron-diffraction measurements indicate that, in the molecule $HN^1N^2N^3$, the interatomic distances are $N^1N^2 = 1{\cdot}24_7 \pm 0{\cdot}01$ A., and $N^2N^3 = 1{\cdot}13_6 \pm 0{\cdot}01$ A.[40] The details of the structure of hydrogen azide were improved by a study of the microwave spectrum.[41] The interatomic distances were found to be: $HN^1 = 1{\cdot}021 \pm 0{\cdot}01$ A., $N^1N^2 = 1{\cdot}240 \pm 0{\cdot}003$ A., $N^2N^3 = 1{\cdot}134 \pm 0{\cdot}003$ A., and the angle HN^1N^2 was found to be 112° 39′ ± 30′. These values agree well with the assumption of equal resonance between the structures:



$$H-\ddot{N}=\overset{+}{N}=\underset{\cdot\cdot}{\overset{-}{N}}: \text{ and } H-\underset{\cdot\cdot}{\overset{-}{\ddot{N}}}-\overset{+}{N}\equiv N:$$

The calculated distances are $N^1N^2 = 1{\cdot}25$ A., and $N^2N^3 = 1{\cdot}12$ A.[42] The value calculated for the bond angle, HN^1N^2, is about 112°, which agrees closely with the observed value. The component of the dipole moment along the approximate figure axis of hydrogen azide is $0{\cdot}847 \pm 0{\cdot}005$ D.[41]

A detailed study of bond-orders, force constants and hybridization was used to obtain indications of the electronic binding in hydrogen azide, in terms of molecular orbitals.[43] The central nitrogen atom was found to be quadrivalent. Further molecular orbital and valence-bond calculations have been used to describe the structure of hydrogen azide.[44] The heat of formation and the interatomic distances of hydrogen azide have been calculated and found to be in agreement with experimental values.[44] The derived figures show that the $—N{\equiv}N$ bond is much weaker (180·9 kcal.) than the $N{\equiv}N$ bond (226 kcal.) and it was assumed that it is this large difference in the heats of formation of hydrogen azide and its decomposition products that is responsible for its explosive properties.

In a study of the effect of resonance stabilization on parachor values, the structure of hydrogen azide has been discussed.[45, 46]

Although the crystal structure of hydrogen azide has not been investigated, the isoelectronic compound, HCNO, was found to be orthorhombic, with its molecules linked together by N–H...N hydrogen bonds, in infinite zigzag chains.[47] Solid hydrogen azide probably exhibits similar bonding and will show an extreme departure from the ionic state.

Dissociation and Decomposition of Hydrogen Azide

DISSOCIATION IN AQUEOUS SOLUTION

Hydrogen azide dissolves in water with the formation of a weakly acidic solution. The dissociation constant of aqueous hydrogen azide has been measured by means of a glass electrode, and the following values obtained: $2{\cdot}56 \times 10^{-5}$,[48] $2{\cdot}16 \times 10^{-5}$ at 25°.[49] Using a glass electrode the pK value of aqueous hydrogen azide was found[50] to be 4·77 at 25°C. A cell without a liquid junction was used to obtain a value of $1{\cdot}91 \times 10^{-5}$ at 25°, and from this ΔF°_{298} for the equation:

$$HN_3 \rightarrow H^+ + N_3^-$$

was calculated to be 6442 g.-cal.[49] Several solutions of hydrogen azide of different concentrations, prepared by the interaction of sulphuric acid and sodium azide, were kept in darkness in a closed vessel and titrated electrometrically.[51] From a series of determinations the dissociation constant of aqueous hydrogen azide was found to be $2{\cdot}8 \times 10^{-5}$.

The basic dissociation constant of $H_2N_3^+$ was found by the equilibration of hydrogen azide between chloroform and sulphuric acid.[52] From the concentrations of hydrogen azide and $H_2N_3^+$ in the two phases the pK value was found to average $-6{\cdot}21$ over the range 77·96–84·56% H_2SO_4.

Hydrogen azide can be decomposed by thermal, photochemical and electrolytic methods. It seems to be generally agreed that the initial step in all these methods is the rupture of the longest nitrogen–nitrogen bond, thus affording the imine radical, HN:, and elementary nitrogen[53–57]:

$$HN_3 \rightarrow HN{:} + N_2$$

The nature of the products from a particular method of decomposition depends on further reactions of the imine radical, which can lead to nitrogen, hydrogen, ammonia and (if water is present) to hydroxylamine, and (in the presence of benzene) to aniline etc.

THERMAL DECOMPOSITION

The thermal decomposition of hydrogen azide at 290° and a few cm. of Hg pressure proceeds with measurable velocity.[54, 55] The decomposition is catalysed by the Pyrex walls of the reaction vessel,[58] and markedly so by traces of impurities.[54] The reaction is heterogeneous, first order, and yields at least 94% of the theoretical quantity of ammonia plus nitrogen.[54] When the decomposition is accomplished by the passage of hydrogen azide at a low pressure, e.g. 0·1 mm. Hg, through a quartz tube at 1000°, and the products immediately collected on a surface cooled with liquid nitrogen, the overall reaction appears to be:

$$6HN_3 \rightarrow 7N_2 + H_2 + (NH)_4$$

The entity $(NH)_4$ is a blue paramagnetic solid, which changes into ammonium azide, NH_4N_3 at $-150°$ and $-125°$, for small and larger deposits respectively.[55,56] The half-life of the imine radical, HN:, is estimated to be 9×10^{-4} sec., when hydrogen azide is passing through a 1·7 cm. quartz tube at 1060° at a rate of 10 m.sec.$^{-1}$ and at a pressure of 0.07 mm.[55]

PHOTOCHEMICAL DECOMPOSITION

Hydrogen azide solutions are immediately decomposed by illumination with a quartz mercury lamp.[59] The amounts of nitrogen, hydroxylamine, ammonia and hydrazine formed at various pH values were quantitatively measured. Whereas brief illumination of hydrogen azide gave a non-condensable (liquid air) gas, longer periods produced a white solid, assumed to be ammonium azide, simultaneously with the formation of nitrogen and hydrogen.[60] The decomposition of hydrogen azide, over the range 0·328 to 131·0 mm. Hg, by radiation of wave-length 1990 A., has been studied and a mechanism proposed.[57] Irradiation of aqueous hydrogen azide by light of wave-length 2537 A., showed, by means of a graph of yield against temperature, an induction period followed by a rapid increase to a maximum, and finally a decrease.[61] The large yields observed at the maximum were explained on the basis of a chain reaction for the decomposition. The mechanism of this chain reaction has been further discussed and investigated; it is postulated that the chain carrier is excited nitrogen, N_2^*.[62] Photolysis of hydrogen azide, at 2537 A., during and after deposition of it at 4°K. and 77°K., gives the same products as the vapour-phase decomposition.[63] The analogy between the initial reactions of nitrous oxide, diazomethane and hydrogen azide, when exposed to ultra-violet radiation, has been reviewed and discussed[64]:

$$HN_3 \rightarrow HN\colon + N_2$$
$$N_2O \rightarrow O + N_2$$
$$CH_2N_2 \rightarrow CH_2\colon + N_2$$

The photosensitized decomposition of hydrogen azide, at 0·3 to 20 mm. Hg, gives hydrogen, nitrogen, ammonia and ammonium azide initially; it closely parallels the photochemical decomposition.[65]

ACTION OF ELECTRIC DISCHARGE

Hydrogen azide, when passed through an electric discharge tube, at 0·1 to 0·01 mm. Hg, decomposes and, on a cold (liquid nitrogen) surface placed three inches from the end of the tube, a blue solid is deposited.[66] This solid has a transition point at −125°, where white ammonium azide is formed, thus indicating that the solid is the same as that produced in the thermal decomposition.[56] The collection of the decomposition products at 4°K., and 77°K. in an optical cell enabled an infra-red examination to be made[63]; the blue solid was found to contain a substantial quantity of undecomposed hydrogen azide, and the absorption spectrum at low temperature showed the presence of ammonium azide. In the absence of a discharge, deposition of hydrogen azide at 77°K. gave a clear, colourless glass which became polycrystalline at 148°K. Since no increase was observed in the intensities of the ammonium azide band or any other products, the concentration of radicals, which had been stabilized at the lower temperatures, was very small. The products of discharges through hydrogen azide have been trapped at 4·2°K., and examined spectroscopically.[67]

FLASH PHOTOLYSIS

In the high-intensity flash photolysis of hydrogen azide in the presence of an excess of inert gas, the absorption spectra of the radicals NH and NH_2 were observed; in addition a new absorption was detected at about 2700 A.[68] When the hydrogen azide was replaced by deuterium azide no shift of the new absorption was observed, and it was assigned to the N_3 radical, which is isoelectronic with CO_2^+. The mechanism proposed for the flash photolysis is as follows:

$$HN_3 + h\nu \rightarrow HN + N_2$$
$$HN + HN_3 \rightarrow NH_2 + N_3$$
$$NH_2 + HN_3 \rightarrow NH_3 + N_3$$
$$2N_3 \rightarrow 3N_2$$

Thus: $$3HN_3 \xrightarrow{h\nu} NH_3 + 4N_2$$

The photolysis of hydrogen azide in solid nitrogen at 20°K., in the presence of oxygen, affords *cis-* and *trans*-nitrous acid.[69] The identification was based on the infra-red detection of features of the species, HONO, DONO and $H^{18}O\,N^{18}O$. Reaction of the imine radical with the oxygen was held responsible for the formation of nitrous acid:

$$HN\!:+O_2 \rightarrow HONO$$

It has been found that hydrogen azide is decomposed by non-luminous active nitrogen; the presence of hydrogen leads to the formation of ammonia, and the presence of benzene affords aniline.[70] On the basis of these experiments it was suggested that the imine radical, well-known spectroscopically, is sufficiently stable to act as a chemical intermediate.

The reactivity of the hydrogen azide ion has been explained on the basis that the absorption of energy separates the charges still further, thus producing a more reactive species.[71]

Electrolysis of aqueous hydrogen azide is accompanied by the emission of ultraviolet radiation; this emission is increased several hundredfold if nitrogen or hydrogen is bubbled through the anolyte, but argon and nitrous oxide have no effect, and oxygen inhibits the emission.[72] A chain mechanism involving N_2^+, N, NH and H has been proposed for the phenomena.

EXPLOSIVE DECOMPOSITION

The explosive decomposition of hydrogen azide has attracted interest ever since it was first discovered. It has been suggested that, in the explosion, reaction chains are propagated by atoms of nitrogen.[73, 53]. The velocity of detonation of hydrogen azide, pure and when admixed with hydrogen, has been measured by photographing the flame on moving film.[74] In the radiation emitted by the explosive decomposition of hydrogen azide, five bands were ascribed to the imine radical.[4] A lower limit of 5 mm. Hg pressure was observed for the explosive decomposition of hydrogen azide by means of an electric spark.[75] The explosion was markedly inhibited by the addition of nitrogen, argon and particularly hydrogen to the hydrogen azide. The critical limits of both pressure and temperature, for the explosive decomposition of hydrogen azide, have been studied.[75] Induction periods of one-fifth of a second were observed, and a final pressure increase of 100%. The reactions involved were given as:

$$HN_3 \rightarrow HN\!:+N_2;\quad \Delta H \text{ approx. 5 kcal./mole}$$

$$HN\!:+HN\!: \rightarrow N_2+H_2;\quad \Delta H\ -154 \text{ kcal./mole}$$

$$HN\!:+HN_3 \rightarrow 2HN\!:+N_2 \rightarrow 2N_2+H_2;\quad \Delta H\ -149 \text{ kcal./mole}$$

The non-explosive decomposition was also investigated; an induction period of one second was followed by a noiseless white luminescence, and a final pressure increase of 2 to 5% was observed.[76]

Analytical Reactions

The well-known reaction of aqueous hydrogen azide with ferric salts,[34] to give a blood-red coloration, has been used as the basis for the spot-plate detection of the acid; silver salts have also been used.[77] The ferric azide test has been used to detect the presence of hydrogen azide in wine.[78] The typical crystals formed with hydrogen azide and mercuric acetate or hexamethylenetetramine can be used for identification purposes.[32] Aqueous hydrogen azide is said to give a characteristic crystalline product with 1,6-dichlorotetrapyridinecobaltic chloride.[79]

A colorimetric method for the determination of aqueous hydrogen azide involves treatment of a dilute solution of the azide (100 ml) with hydrochloric acid (1 ml) and 0·1 N. ferric chloride (1·5 ml). The resultant solution is compared with a standard solution; the error is said to be less than 0·4%.[80]

Aqueous hydrogen azide reacts with acidic ceric solutions thus:

$$2Ce^{4+}+2HN_3 \rightarrow 3N_2+2Ce^{3+}+2H^+$$

If care is taken to exclude oxygen accurate determinations of hydrogen azide can be made by the determination of the excess of ceric ion iodimetrically.[81]

Acidic solutions of hydrogen azide can be determined by a combination of permanganimetry and iodimetry.[82]

Organic Chemistry of Hydrogen Azide

Hydrogen azide, as befits a very reactive molecule, takes part in a wide variety of organic reactions. In some of these reactions it functions as an acid; it also reacts as a covalent compound as in cyclization reactions, and in other ways.

Azides of organic bases can be prepared in various ways. Thus the sulphate of the base can be treated with barium azide, any salt of the base can be treated with sodium azide, or, most satisfactorily, the free base can be treated with aqueous hydrogen azide.[83] Further, azides of alkaloids can be prepared by the reaction of the alkaloid with potassium azide in dilute aqueous acetic acid.[84] Quaternary ammonium azides can be prepared by the addition of aqueous or alcoholic hydrogen azide to a similar solution of the free base; alternatively, hydrogen azide vapour, in nitrogen, can be passed into an aqueous solution of the base.[85]

Hydrogen azide, in aqueous ethanol, reacts with aromatic *C*-nitroso compounds, with the evolution of two molecules of nitrogen and the formation of an azide[86, 87]:

$$\mathrm{ArNO + 2HN_3 \rightarrow ArN_3 + H_2O + 2N_2}$$

The reaction is of wide application and very high yields of azides have been obtained. The nature and position of substituents in the aromatic nucleus apparently have little or no effect on the reaction.[87] When the above reaction is attempted with aliphatic *gem*-chloronitroso compounds, mixtures of ketones, chloro-olefines, and occasionally chloroazides, are obtained.[88]

The first step in the decomposition of hydrogen azide by concentrated sulphuric acid was assumed by Schmidt to be the formation of the imine radical :NH.[20] To capture this radical Schmidt added to the reaction mixture a wide variety of compounds containing the carbonyl group, and discovered what is now known as the Schmidt reaction. The following equations are representative of these reactions.

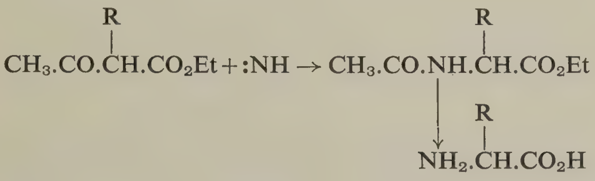
Ketones to amides:

$$\mathrm{R_2CO + :NH \rightarrow R.CO.NH.R}$$

Aldehydes to nitriles or N-formylamines:

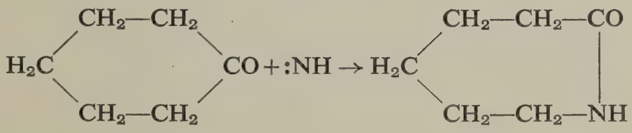
$$\mathrm{R.CHO + :NH \rightarrow RCN + H_2O \text{ or } R.NH.CHO}$$

α-Keto-acids to α-amino-acids:



$$\mathrm{CH_3.CO.\overset{R}{\overset{|}{C}}H.CO_2Et + :NH \rightarrow CH_3.CO.NH.\overset{R}{\overset{|}{C}}H.CO_2Et \;\downarrow\; NH_2.\overset{R}{\overset{|}{C}}H.CO_2H}$$

Cyclic ketones to lactams (cyclic amides):

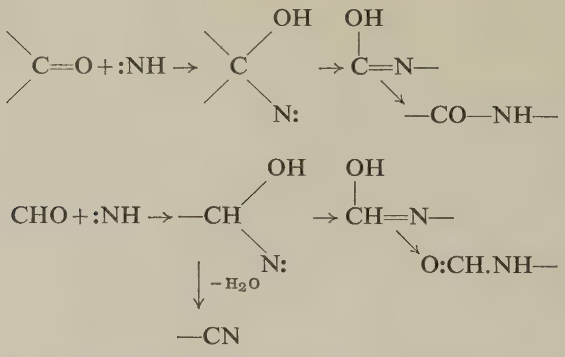


Excess of hydrogen azide with aldehydes or ketones, acyclic or cyclic, yields tetrazole derivatives.

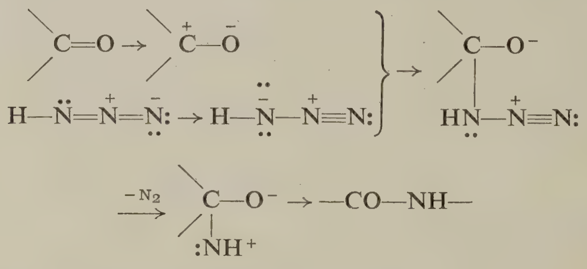
Aromatic hydrocarbons to amines:

$$Ar\text{-}H + :NH \rightarrow Ar.NH_2$$

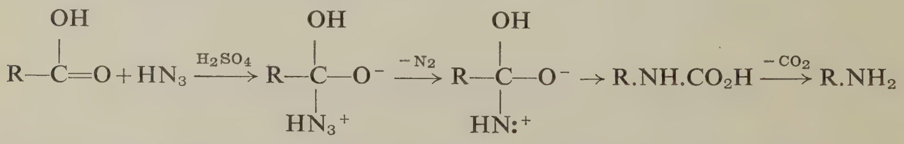
Schmidt postulated that, with the carbonyl compounds, an intermediate addition product is formed which either undergoes a Beckmann transformation or, with aldehydes, loses a molecule of water:



An alternative mechanism was put forward, based on the addition of a molecule of hydrogen azide to the compound as the first step.[22] This mechanism has been elaborated several times. Thus it has been suggested that the sulphuric acid activates both the carbonyl compound and the hydrogen azide; the interaction of these two entities is then followed by elimination of nitrogen, and then the intermediate, which is now similar to that proposed by Schmidt, undergoes rearrangement[89]:

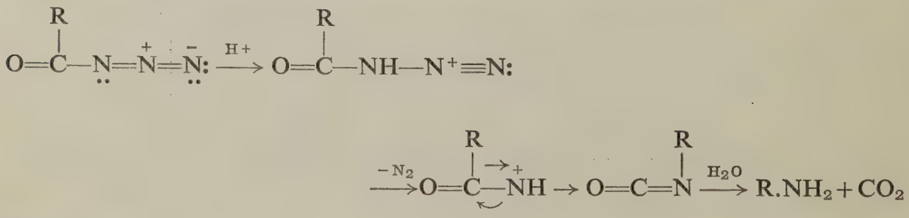


A similar scheme was proposed for carboxylic acids:



$$R-\overset{OH}{C}=O + HN_3 \xrightarrow{H_2SO_4} R-\underset{HN_3^+}{\overset{OH}{C}}-O^- \xrightarrow{-N_2} R-\underset{HN:^+}{\overset{OH}{C}}-O^- \rightarrow R.NH.CO_2H \xrightarrow{-CO_2} R.NH_2$$

A more recent proposal for the last case is that, initially, an acyl azide is formed, which decomposes, via a nitrogenium ion, to an *iso*cyanate.[90] The latter is then decomposed, as in the Hofmann, Lossen and Curtius reactions, to a primary amine:



$$O=\overset{R}{C}-\ddot{N}=\overset{+}{N}=\overset{-}{\ddot{N}}: \xrightarrow{H^+} O=\overset{R}{C}-NH-N^+\equiv N:$$

$$\xrightarrow{-N_2} O=\overset{R}{C}-\overset{+}{N}H \rightarrow O=C=\overset{R}{N} \xrightarrow{H_2O} R.NH_2+CO_2$$

As outlined earlier, hydrogen azide in the presence of concentrated sulphuric acid converts ketones into amides. If the ketone is unsymmetrical two different products are possible:

$$\text{R—CO—R}' \rightarrow \text{R—CO—NH—R}' \text{ or } \text{R—NH—CO—R}'$$

In a series of dialkyl, alkyl-aryl and diaryl ketones it was found that the higher alkyl, aryl and substituted aryl groups migrate preferentially.[91] Further investigations on phenyl para-substituted phenyl ketones and alkyl-aryl ketones indicated that it is largely steric factors which determine the preferred product.[92, 93] That it is the bulkier group which migrates was confirmed by a study of benzoyl- and naphthoylbenzoic acids, although several exceptions were observed.[94] Similar results were observed with other acylbenzoic acids and alkylidene phthalides.[95] In several *cyclo*propyl ketones, the *cyclo*propyl group does not preferentially migrate, whereas in 1-phenyl*cyclo*propyl ketones, migration of the three-membered ring predominates.[96] *tert.*-Butyl alkyl ketones give mixtures of several products; the predominant reaction is cleavage of the intermediate ion with formation of *tert.*-butyl derivatives of the hydrocarbon solvent.[97] The Schmidt reaction enables cyclic ketones to be converted into cyclic amides ('lactams') in high yields.[98] In a study of the Schmidt reaction with 2-substituted cyclic ketones it was shown that the predominant lactam is that in which the NH group lies between the carbonyl group and the substituent[99, 100, 101]; 2-chloro*cyclo*hexanone is unusual in that it gives 3-chloro-2-oxohexamethyleneimine.[99] Substituted fluorenones give mixtures of the two possible isomeric phenanthridones.[102] The sodium salts of secondary nitro-compounds are hydrolysed by sulphuric acid to ketones, i.e., the 'Nef reaction', and if sodium azide is present the ketone is immediately converted into an amide.[103] α-Diketones such as benzil react with hydrogen azide in sulphuric acid yielding, as the main product, a compound with an NH group on each side of one of the carbonyl groups.[104] Cyclic α-diketones such as phenanthrenequinone,[105, 106] retenequinone,[105–109] and chrysenequinone,[105] react with two equivalents of hydrogen azide to form a phenanthridone, i.e. the overall effect is that one of the carbonyl groups is replaced by an NH group. The course of this reaction has been thoroughly studied.[106–109] In substituted 3:4-anthraquinones the quinone ring is enlarged by the insertion of an NH group between the two carbonyl groups.[110] Acenaphthenequinone appears to give a similar product initially, although the product isolated is either naphthalamic acid or naphthalic acid anhydride, according to the conditions of isolation.[111] Isatin does not give a cyclic product but yields anthranilamide.[105] Dialkyl or aryl-alkyl β-diketones react vigorously in the Schmidt reaction to give oxazoles; diaryl β-diketones do not react.[109] On the other hand γ-diketones do not form cyclic products but give derivatives of succinic acid diamide, e.g., 1,2-dibenzoylethane yields succinic acid dianilide.[112] Benzo- and naphtho-1,4-quinones decompose under the conditions of a Schmidt reaction; alkyl substituted benzo-1,4-quinones give products which probably involve ring contraction.[113, 114] Anthraquinone, on the other hand, behaves like a normal cyclic ketone inasmuch as one of the carbonyl groups is converted into an amide, whilst the other remains untouched.[115] The reactions of *p*-quinones and *p*-quinone-diimines with hydrogen azide in conditions other than those used in the Schmidt reaction have been investigated.[116–119]

Aromatic aldehydes afford mainly N-formyl anilines in the Schmidt reaction at high acid concentration; as the concentration is reduced a greater proportion of the corresponding nitrile is formed. With *p*-methoxy and *p*-nitro substituents the nitrile is the main product throughout.[120]

The reaction of hydrogen azide with styrene oxide has been studied.[120]

Carboxylic acids readily participate in the Schmidt reaction to give an amine with one fewer carbon atom.[121–123]

$$\text{R.CO}_2\text{H} + \text{HN}_3 \rightarrow \text{R.NH}_2 + \text{N}_2 + \text{CO}_2$$

A wide variety of acids has been used and several studies have been made of the effect that the nature of the group R has on the yield of amine.[89, 92, 124] In substituted malonic acids only one of the *gem*-carboxyl groups is eliminated and the products are α-amino acids.[125] Acids in the terpene series have been converted into amines in very high yields.[126] If the acid has the appropriate structure cyclization sometimes occurs. For example diphenic acid yields a mixture of 2,2′-diaminodiphenyl and phenanthridone.[105, 110] Acid anhydrides usually yield mixtures of the various possible products.[105,127] Diphenic acid anhydride yields phenanthridone.[105]

The behaviour of alcohols in the Schmidt reaction has been studied mainly in the cyclic series. Thus the conversion of a large series of 9-fluorenols into phenanthridines has been studied.[128–130] A series of monocyclic alcohols gave the corresponding ketones together with amines and other products formed by ring enlargement.[131] Triphenylmethanol gives triphenylmethyl azide but from diphenylmethanol a mixture of aniline, benzene and diphenylmethyl azide is obtained.[128]

The behaviour of 1,1-diarylethylenes in the Schmidt reaction has been investigated. The major product is an aryl methyl ketone; when two different aryl groups are present varying amounts of the two possible ketones are produced.[132, 133] If trichloracetic acid is used instead of sulphuric acid the 1,1-diaryl-1-azidoethane can be isolated; the latter decomposes when treated with sulphuric acid.[134]

In the presence of a weaker acidic catalyst hydrogen azide adds to ethylenic bonds, isolated[135] or conjugated,[136] to form azides.

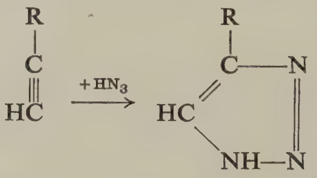
As mentioned earlier Schmidt isolated aniline from the reaction between hydrogen azide and sulphuric acid in benzene.[20] This reaction has been extended to other aromatic hydrocarbons, e.g., *p*-xylene gives *p*-xylidine, etc.[137–139] The mechanism of aromatic amination by hydrogen azide has been studied and it has been suggested that it operates in a way different from that of the Schmidt reaction, possibly via the radicals $:NH$ or $:\overset{+}{N}H_2$.[140] Usually only low yields are obtained in aromatic amination; mesitylene, however, is unusual in giving appreciable yields of aminated products.[141] An investigation of this reaction gave results which, whilst not revealing the exact nature of the intermediate species, indicated that the -onium ion, $N{=}\overset{+}{N}{-}NH_2$ reacts with an aromatic nucleus to afford nitrogen and $:NH_2^+$ is the transient electrophile responsible for the amination.

Sulphoxides participate in the Schmidt reaction with the formation of sulphoximines[142, 143]:

$$R_1R_2SO \rightarrow R_1R_2S(O)NH$$

Ethyl 2-2′-methylthioethyl-acetoacetate is attacked in two places during a Schmidt reaction giving an acetamido-sulphimine; baryta converts this product into an amino-acid sulphoxide.[144]

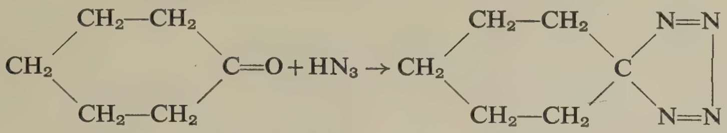
Hydrogen azide reacts with activated multiple bonds usually yielding cyclic products. These products can be triazoles, tetrazoles or pentazoles if the atoms forming the multiple bond are both carbon, one carbon and one nitrogen, or both nitrogen, respectively. Thus substituted acetylenes give rise to triazoles, i.e.,



$R = CHO$,[145] alkyl,[146] OEt.[147]

Dimethyl acetylenedicarboxylate is said to yield an azide.[148]

A wide variety of compounds react with hydrogen azide to give tetrazoles. In particular compounds which contain adjacent double bonds, such as, $=C=N-$, $O=C=C<$, $O=C=N-$, $S=C=N-$, $-N=C=N-$, $S=C=S$, readily give tetrazoles.[149–152] Tetrazoles are also formed during the reaction between hydrogen azide and azodicarboxylic esters,[153] and *iso*nitriles and hydrazones.[154] Tetrazole oxides are formed by the reaction of hydrogen azide with nitrolic acids.[155] Cyclic ketones react with hydrogen azide to give a *spiro*-tetrazole, e.g.[156]:



Compounds of this type can also be prepared from ketoximes, via the sulphonic ester and a Beckmann rearrangement in the presence of a mercaptan, followed by treatment with hydrogen azide.[157]

Although nitriles do not react with hydrogen azide as such, they do react under the conditions of a Schmidt reaction.[158] Thus benzonitrile and hydrogen azide, when treated in benzene with concentrated sulphuric acid, yield 1-phenyl-5-aminotetrazole.

Early attempts to synthesize the pentazole nucleus, e.g. from hydrogen azide and diazomethane, gave nitrogen and an azide, in this case methyl azide.[159] However, hydrogen azide has been caused to react with diazonium ions to give, for example, phenylpentazole.[160–162]

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SECTION XIX

THE METALLIC AZIDES

BY K. G. MASON

PREPARATION

Simple Azides

AMMONIUM AZIDE AND THE ALKALI-METAL AZIDES

When pure dry ammonia is led into a solution of hydrogen azide in ether, pure ammonium azide, which is only sparingly soluble in this solvent (6×10^{-3} g./100 ml.), separates in good yield.[1] Alternatively, ammonium azide can be made in high yield (85–95%) by heating a dry mixture of ammonium nitrate and sodium azide to 200°; at temperatures above 133° ammonium azide sublimes and so can be separated from the sodium nitrate produced concomitantly.[1] The second method is preferably restricted to small-scale preparations (maximum, 5 g.). However, larger weights can be safely handled by causing sodium azide and ammonium chloride to react in formdimethylamide at 100°.[2] At the completion of the reaction the ammonium azide and formdimethylamide are distilled *in vacuo* (60–70°/30–5 mm. Hg); when the distillate is cooled the azide separates. Ammonium azide can be prepared by mixing gaseous hydrogen azide with an excess of ammonia, cooling to −78° and evacuating the reaction vessel.[3] Ammonium azide is formed when the products from the decomposition of hydrogen azide in a glow discharge, having been collected in a liquid-air trap, are allowed to warm to −125°.[4]

Lithium azide is said to be produced when oxygen-free nitrogen is passed over lithium heated to 500–600°.[5] Lithium azide can be prepared by the interaction of sodium azide and lithium chloride in an aqueous-alcoholic solution.[6] The preparation of anhydrous lithium azide is hindered by the existence of a stable monohydrate; the use of ethereal or concentrated aqueous solutions is recommended, and prolonged drying over phosphorus pentoxide is also advised.[7] Alternatively, ethanol can be used as solvent in the following method by which 99·5% pure lithium azide can be prepared: Sodium azide and lithium sulphate monohydrate (10% excess) are dissolved in a small amount of water and a five-fold volume of 96% ethanol is added; after ten minutes the precipitate is filtered and then washed with ethanol. The combined filtrate and washings are evaporated nearly to dryness on a water-bath and the residue dried at 80°.[8]

If a mixture of lithium chloride (8·5 g.), sodium azide (15 g.), and methanol (200 ml.) is boiled under reflux for five hours, refrigerated and then filtered, the filtrate is a 0·92 M. solution of lithium azide in methanol.[9]

Lithium azide is also obtained when lithium borohydride and hydrogen azide react at −80° (see page 19).

A starting-point for the preparation of many azides is sodium azide. The convenient preparation of this compound from sodamide and nitrous oxide, or sodium, ammonia and nitrous oxide, first described by Wislicenus (Mellor, VIII, 345), has been studied in several ways. Thus the use of the nitrogen isotope ^{15}N and isotopic analysis of the product indicates that the nitrogen atom in the sodamide provides a terminal atom in the azide ion. Further, two products are formed in different proportions depending upon whichever isotopic form of nitrous oxide is used; this suggests that two simultaneous reaction mechanisms are operative[10–12]:

$$(a)\quad NaNH_2+O^{15}NN \xrightarrow{-H_2O} \left\langle \begin{array}{ll} \rightarrow Na^{15}NNN & 80\% \\ \rightarrow NaN^{15}NN & 20\% \end{array} \right.$$

$$(b)\quad NaNH_2+ON^{15}N \xrightarrow{-H_2O} \left\langle \begin{array}{ll} \rightarrow Na^{15}NNN & 25\% \\ \rightarrow NaN^{15}NN & 75\% \end{array} \right.$$

This study was extended to the amides of lithium, potassium, rubidium, cæsium, calcium, strontium, barium and zinc.[12] It was found that as the radius of the cation decreased so the proportion of the centrally labelled azide ion (in reaction (*b*)) increased. This was taken to indicate that the polarization and relative sizes of the reactants determined the reaction mechanism, and, in contradiction to earlier postulates, the ion $[O—N{=}N—N—H]^{--}$ was suggested as the intermediate product.[12] Mass-spectrographic analyses of the products from the reactions between sodamide and $N^{15}NO$, ^{15}NNO, and $^{15}N^{15}NO$ show that in the first two cases 41% and in the last case 80·5% of the nitrogen is the ^{15}N isotope in the azide. The isotopic exchange:

$$[^{15}NNN]^- \rightleftharpoons [N^{15}NN]^-$$

does not exist in the melt, even in the case of rubidium azide which is stable up to 350°. The centrally labelled azide, $NaN^{15}NN$, can be synthesized as follows[13]: *p*-Nitroaniline is diazotized with $[^{15}N]$ nitrous acid and the solution treated with bromine, whereupon the tribromide, $p\text{-}NO_2.C_6H_4.N^{15}NBr_3$, is obtained. Addition of this tribromide to ammonium hydroxide covered with ether, followed by steam-distillation, gives $p\text{-}NO_2.C_6H_4.N^{15}NN$, m.p. 71–2°. The *p*-nitrophenyl azide is heated with powdered sodium hydroxide for 2 hr. and the mixture is acidified and distilled; neutralization of the distillate with aqueous sodium hydroxide gives $NaN^{15}NN$.

The reactions between sodium, ammonia, and nitrous oxide in liquid ammonia have been extensively studied. In a stainless-steel bomb at 19·2–28·8 atm., and −40 to 30° nearly theoretical yields are produced after 16–25 hr., according to the following equation[14, 15]:

$$4Na+3N_2O+NH_3 \rightarrow NaN_3+3NaOH+2N_2$$

If previously prepared sodamide is used the reaction is slower, but consumption of raw materials is less and the yield is still over 95% of that predicted by the equations:

$$2Na+2NH_3 \rightarrow 2NaNH_2+H_2$$
$$2NaNH_2+N_2O \rightarrow NaN_3+NaOH+NH_3$$

The use of solid, liquid, or gaseous nitrous oxide reveals that the same reaction mechanism applies in each case.[16] The conversion of sodamide into sodium azide with nitrous oxide in liquid ammonia is of considerable industrial importance and has been studied extensively.[17–21] It has been established that a double salt, NaN_3, $NaOH$, is the main component of the crude reaction product and that the rate of formation of this salt increases as the concentration of sodium azide increases. It was found at the same time that under these conditions the solubility of sodium in liquid ammonia decreases. The stability of the double salt in liquid ammonia decreases both when the temperature is lowered, and in the presence of 10–25% of water (i.e., ~2–3 times as much water as sodium hydroxide). In the presence of this quantity of water complete decomposition occurs at 0°. This decomposition is also promoted by ammono-acids such as urea and acetamide, whereas ammono-bases, e.g. sodamide, promote the formation of the double salt. Solid sodium azide, with a purity of at least 99%, can be produced in over 95% yield by the use of 5–15 g. of partly hydrated liquid ammonia for every gram of sodium azide in the crude product. The addition of ammonium chloride to the reaction liquor is said to promote high yields and to facilitate production of a pure product.[22]

Since sodium azide is used so extensively for the production of other industrially important azides several methods have been used for its purification. Thus, carbonate can be removed by the use of the usual agents such as barium hydroxide.[23] If crude sodium azide is made into a paste with water containing 2–4% of sodium hydroxide and then treated several times with anhydrous acetone the residue is pure sodium azide.[24] Crude sodium azide containing 24–92% of azide can be improved to a state of 95% purity by dissolution in liquid ammonia at −33°, filtration, and evaporation.[25] A second similar treatment raises the purity to 99·5%. When very pure sodium azide is required repeated recrystallization from water followed by precipitation with ethanol from a solution made slightly acid with aqueous hydrogen azide is recommended.[7]

The reaction between sodamide and nitrous oxide is said to be conveniently accomplished in a hydrocarbon oil or other inert liquid at 150–180°.[26]

Large crystals of sodium azide (4 × 6 × 1 mm.) have been obtained in a special apparatus, in which a supersaturated aqueous solution of sodium azide is circulated over a seed crystal.[27] Large crystals of potassium azide (6 × 6 × 3 mm.) have been prepared simply by placing a saturated solution of the azide in a polyethylene bottle the cap of which had a small hole; after several months half of the solution had evaporated and often to be found in the residue were several large crystals.[27] This method is not suitable for sodium azide because dendrites appear and these prevent the extended growth of any one crystallite.

Since hydrogen azide has several unpleasant characteristics the preparation of azides based on the reaction between hydrazine and nitrous acid (cf. Mellor, VIII, 345) has been extended. A convenient preparation of sodium and potassium azides from the corresponding ethoxide, hydrazine hydrate, and butyl nitrite has been described.[1] Other alkyl nitrites have also been used.[28, 29]

Experimental details for the preparation of potassium amide and potassium azide by the Wislicenus method have been published.[5]

Sodium, potassium, rubidium, and cæsium react with nitrogen, which has been activated by an electrical discharge, to form azides.[30] Except in the case of sodium the products are contaminated with small quantities of nitrides. With lithium no azide was found and only a small amount of nitride was produced.

The preparation of potassium, rubidium, and cæsium azides from the corresponding hydroxide and aqueous hydrogen azide has been described.[31] After neutralization and concentration, the solution is treated with ethanol whereupon the metal azide is obtained as a colourless microcrystalline solid in high yield. The method can also be adapted to effect the purification of technical sodium azide. Rubidium and cæsium azides are prepared by causing their carbonates to react with concentrated aqueous hydrogen azide and evaporating the mixtures to dryness several times, followed by precipitation with ethanol from a solution slightly acidified with hydrazoic acid. Rubidium azide can be prepared by double decomposition between 16% aqueous barium azide and rubidium sulphate.[32]

BERYLLIUM, MAGNESIUM, AND THE ALKALINE-EARTH METAL AZIDES

Beryllium azide, $Be(N_3)_2$, has been prepared by the addition of an excess of hydrogen azide dissolved in anhydrous ether to dimethylberyllium cooled in liquid nitrogen and then allowing the mixture to warm up.[33] At the melting-point of the solvent (−116°) a rapid reaction occurs; methane is evolved and a white solid separates. Removal of the ether and excess of hydrogen azide in high vacuum affords beryllium azide as a white solid soluble in tetrahydrofuran and insoluble in ether. Beryllium azide is insensitive to shock and detonates weakly in a flame; it is easily hydrolysed by water.

Magnesium azide, $Mg(N_3)_2$, can be efficiently prepared in a similar manner from diethylmagnesium in an ether–dioxan solution.[34] In this case evolution of ethane and the separation of a white solid begin just below 0°. The azide, isolated as above, is insoluble in tetrahydrofuran and in ether and resembles beryllium azide in that it detonates only slightly in a flame and is sensitive to moisture. Magnesium azide cannot be volatilized in high vacuum at room temperature and separates from water only as $Mg(OH)N_3$.

The alkaline-earth metal azides are prepared easily from the corresponding hydroxide and hydrogen azide. The hydrogen azide can be used as its aqueous solution obtained by distillation *in vacuo* from sodium azide and sulphuric acid,[6] or by passing a stream of carbon dioxide-free air[35] or nitrogen[36] into the sodium azide–sulphuric acid mixture and thence into a solution of the metal hydroxide. The azides can be isolated by concentration,[35] or by the addition of ethanol,[31] followed by filtration and washing with ethanol, and are best stored slightly moistened with ethanol.[35] If the anhydrous azide is required the above product is washed with ether and stored in a vacuum desiccator.[31]

The preparation of calcium azide is complicated by the facts that this is the most soluble of the alkaline-earth metal azides in ethanol and if the aqueous solution is concentrated a hydroxy salt is obtained. The azide can be prepared by the distillation of aqueous hydrogen azide directly on to the hydroxy azide, followed by precipitation with acetone and ether.[7] The preparation of the isotopically labelled calcium azide, $Ca(^{14}N^{15}N^{14}N)_2$, has been reported: calcium amide is allowed to react with highly enriched nitrous oxide in which the [^{14}N] nitrogen and [^{15}N] nitrogen contents are nearly equal.[37]

The preparation of strontium azide is rendered difficult by its extreme sensitivity to hydrolysis.[38] The azide can be obtained by dissolving the carbonate in 14% aqueous hydrogen azide, repeatedly evaporating to dryness with fresh solution and precipitating with ethanol.[7]

Barium azide is easily prepared from potassium azide and barium perchlorate,[6, 38] and, on the kilogram scale, from a mixture of ethyl nitrite, hydrazine, and barium hydroxide cooled to $-15°$.[6, 38] Barium azide is said to be a possible product when a pure barium film is 'flashed' in nitrogen at 5×10^{-3} mm. Hg pressure.[39]

BORON, ALUMINIUM, GALLIUM AND THALLIUM AZIDES

When the hydrides of boron,[40] aluminium,[41] and gallium[42] are caused to react with hydrogen azide in ether at very low temperatures the corresponding azides are formed. The reaction proceeds thus:

$$MH_3 + 3HN_3 \rightarrow M(N_3)_3 + 3H_2$$

In the case of gallium azide the best product had a composition corresponding to the formula $GaH_{0 \cdot 2}(N_3)_{2 \cdot 8}$.

The lithium 'salt' of the complex acid, $HB(N_3)_4$, is formed in the reaction of hydrogen azide with lithium borohydride at 0°[43]:

$$LiBH_4 + 4HN_3 \xrightarrow{0°} LiB(N_3)_4 + 4H_2$$

At lower temperatures ($-80°$) a different reaction occurs with the formation of lithium azide:

$$LiBH_4 + HN_3 \xrightarrow{-80°} LiN_3 + \tfrac{1}{2}B_2H_6 + H_2$$

The corresponding sodium complex compound is produced by the interaction of sodium azide with boron azide[40]:

$$NaN_3 + B(N_3)_3 \rightarrow NaB(N_3)_4$$

Diphenylboron chloride and sodium azide give diphenylboron azide.[44] Thermal decomposition of this compound probably proceeds via two intermediates: (*a*) nitrene, $(C_6H_5)_2BN$:, which can be coupled with dimethylamine to give $(C_6H_5)_2BNH.NMe_2$ for identification purposes, and (*b*) the compound $C_6H_5—B═$

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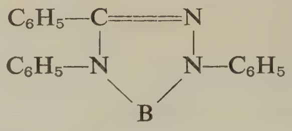
N—C_6H_5 which can be similarly identified by reaction with 1,5-diphenyltetrazole to give the boron heterocycle:



Aluminium azide is formed by the reaction between sodium azide and aluminium chloride in anhydrous benzene.[45] The azide thus produced is insoluble in benzene and is best isolated by the addition of tetrahydrofuran, in which it is soluble. Attempts to use the latter solvent as a reaction medium failed owing to interaction with the freshly formed aluminium azide. On the other hand, later workers prepared an 89% yield of a 0·177 M. solution of aluminium azide in tetrahydrofuran by keeping a solution of aluminium chloride and dry sodium azide in tetrahydrofuran for 15 hr. at room temperature, followed by decantation of the supernatant liquid.[9] Various tetrazoles can be prepared by the addition of organic amides or nitriles to a solution of aluminium chloride in tetrahydrofuran followed by an excess of sodium azide.[45]

When trimethylaluminium is allowed to react with hydrogen azide a single methyl group is retained[46]:

$$Al_2(CH_3)_6 + 4HN_3 \rightarrow 2CH_3Al(N_3)_2 + 4CH_4$$

However, diethylaluminium azide can be prepared by the action of metal azides on the corresponding chloride[47]:

$$(C_2H_5)_2AlCl + MN_3 \rightarrow (C_2H_5)_2AlN_3 + MCl$$

Thallium(I) azide is conveniently prepared from sodium azide and a soluble thallium(I) salt.[48, 49] Thallium(I) azide is insoluble in cold water and thus separates; it can be crystallized from hot water as pale yellow needles and plates.

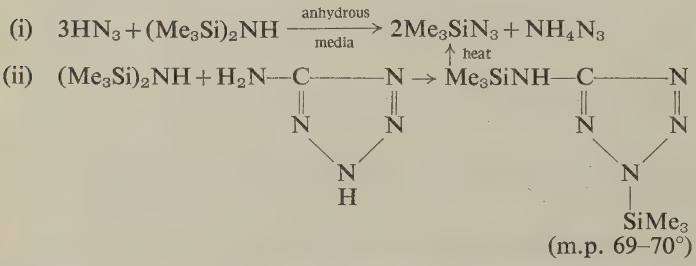
SILICON, TIN AND LEAD AZIDES

Silicon hydride and hydrogen azide dissolved in ether at low temperatures react, with the evolution of hydrogen, to form silicon tetra-azide:

$$SiH_4 + 4HN_3 \rightarrow Si(N_3)_4 + 4H_2$$

A solution of silicon azide in benzene is produced by the reaction of silicon tetrachloride with a suspension of sodium azide in benzene.[50] The colourless crystals of silicon azide are soluble in ether and in benzene and do not sublime at 0° in a high vacuum.

Several organo-silicon azides have been prepared, the first of which was trimethylsilyl azide, a colourless liquid of b.p. 92–3°/760 mm. Hg, attacked by moisture. The following routes were used in the preparation of this compound[51]:



(i) $3HN_3 + (Me_3Si)_2NH \xrightarrow[\text{media}]{\text{anhydrous}} 2Me_3SiN_3 + NH_4N_3$
heat
(ii) $(Me_3Si)_2NH$ + H_2N—C——N → Me_3SiNH—C——N
N N
N
H
N N
N
$SiMe_3$
(m.p. 69–70°)

This preparation was quickly followed by others employing the reaction between divers organosilicon chlorides and alkali-metal azides. Thus trimethyl- and triphenylsilyl azides were quantitatively prepared by the interaction of the corresponding chlorides with a solution of lithium azide in tetrahydrofuran,[52] or with sodium azide in pyridine.[53] Concurrently with these investigations the action of a sodium azide–aluminium chloride mixture dissolved in tetrahydrofuran on various chlorosilanes was being studied.[54] In this way triphenylsilyl azide was prepared, in 90% yield, as a solid of m.p. 81° which could be recrystallized from *n*-hexane. This compound was claimed to be thermally more stable than any previously known covalent azide; only half was destroyed after 10 hr. at 220° in *n*-hexadecane solution. Using the same method of preparation, phenyl dimethylsilyl azide, b.p. 70°/0·15 mm. and trimethylsilyl azide were prepared: for the latter *bis*-(2-methoxyethyl) ether was used as the reaction solvent and the product was obtained only in a purity of 90%.

Organosilicon diazides can be prepared similarly. Thus, diphenylsilyl diazide, b.p. 85–90°/10^{-3} mm., n_D^{20} 1·5887, is prepared from diphenylsilyl dichloride and sodium azide in pyridine.[53] Dimethylsilyl diazide, b.p. 144·3°, can be obtained in 60% yield from the reaction between dimethylsilyl dichloride and sodium azide in a zinc chloride–potassium chloride melt at 230–250°.[55] In the presence of aluminium chloride the following disproportionation reaction is said to occur quantitatively[55]:

$$2Me_3SiN_3 + Me_2SiCl_2 \xrightarrow{AlCl_3} 2Me_3SiCl + Me_2Si(N_3)_2$$

A similar use of the reaction between aluminium chloride and trimethylsilyl azide in order to effect azidation resulted in the quantitative formation of phenylsilyl triazide by the following reaction[56]:

$$3Me_3SiN_3 + C_6H_5{\cdot}SiCl_3 \xrightarrow{AlCl_3} 3Me_3SiCl + C_6H_5{\cdot}Si(N_3)_3$$

The action of sodium azide on methylsilyl trichloride affords a mixture of methylsilyl triazide, methyl(diazidosilyl) chloride, and methyl(azidosilyl) dichloride.[56]

The reaction between stannic chloride and sodium azide in tetrahydrofuran yields, in the first instance, the corresponding azide.[57] However, if an excess of sodium azide is present, this reacts further to give disodium hexa-azidostannate:

$$SnCl_4 + 6NaN_3 \rightarrow Na_2Sn(N_3)_6 + 4NaCl$$

The insolubility of lead azide facilitates its ready preparation by the mixing together of aqueous solutions of a soluble lead salt and a soluble inorganic azide (Curtius, 1891; Mellor, VIII, 353). As a result of the importance of lead azide in the explosives industry the patent literature abounds with variations on this theme, for both batch and continuous processes, and for the control of the physical nature of the product.[58–70] The various industrial processes and laboratory methods have been discussed at length.[71–77] The insolubility of lead azide not only facilitates its preparation but also renders very difficult the preparation of the pure compound. The product is usually contaminated with the cation and anion present in the original solutions, and not only is recrystallization difficult but also spontaneous detonation can occur. Further, if lead oxide is treated with aqueous hydrogen azide then the insoluble lead azide formed on the surface of the particles precludes further reaction. A very elegant solution to this problem has been discovered recently.[78] It has long been known that in acidic solution nitrite and azide ions react together to give nitrous oxide, nitrogen, and water:

$$N_3^- + NO_2^- + 2H^+ \rightarrow N_2O + N_2 + H_2O$$

From this fact it was deduced that an excess of hydrogen azide would have a dual function when added to lead nitrite, i.e., it would destroy the nitrite anion and also react with the lead cation to give lead azide:

$$Pb(NO_2)_2 + 4HN_3 \rightarrow Pb(N_3)_2 + 2N_2 + 2N_2O + 2H_2O$$

A clear, yellow, nitrate-free solution of lead nitrite was prepared by using nitrogen to sweep the vapour evolved from the action of dilute sulphuric acid on aqueous sodium nitrite through a glass-wool plug and into a suspension of lead monoxide in water. This solution was added dropwise to a 10% solution of hydrogen azide in ethanol, whereupon an immediate effervescence took place concurrently with the separation of a white precipitate of lead azide. The product was collected, washed with ethanol and dried *in vacuo* at room temperature. The lead azide (91% yield) was produced in the α-form. It was noticed that a white product was obtained only when spectroscopically pure lead monoxide was used, while a reagent grade gave a slightly yellow product. The advantages claimed for the use of alcoholic hydrogen azide are (*a*) the solubility of the product is lower in this medium thus affording a higher yield and (*b*) the danger of surface hydrolysis and adsorption of carbon dioxide leading to basic lead azides and lead carbonate is minimized.

Two crystalline forms of lead azide have long been recognized, namely the α- and β-forms, which are orthorhombic and monoclinic respectively. α-Lead azide is prepared by crystallization of lead azide from aqueous ammonium acetate, sodium acetate, ammonium chloride, or Rochelle salt solution.[79] The slow cooling of a solution of lead azide in 10% aqueous sodium acetate from 70° to 25° is recommended for the preparation of α-lead azide.[80] The β-form is obtained when a solution of sodium azide is allowed to diffuse into a lead nitrate solution, and usually contains some of the α-form.[79, 80, 81] The growth phenomena when the two solutions are separated by aqueous sodium nitrate have been described.[2]

Lead(IV) oxide and aqueous hydrogen azide react together vigorously but no lead(IV) azide could be isolated from the products.[82] With trilead tetroxide the reaction is less vigorous and gives yellow-red solutions containing compounds affording analyses ranging in composition from PbN_9 to slightly less than PbN_{12}. These solutions decompose spontaneously with concomitant precipitation of lead(II) azide, evolution of nitrogen, and decolorization of the solution. The action of hydrogen azide or acidic azide solutions on lead(IV) salt solutions is said to give red solutions containing lead(IV) azide.[82] An unstable explosive compound, thought to be an ammonium lead(IV) azide, is produced by the addition of light petroleum to the dark-red solution obtained when solutions of diammonium lead hexachloride and sodium azide in ethyl acetate or acetone are mixed.[82]

An improvement to this method consists of the incorporation of a small amount of water in the solvent and the use of a 6:1 molar ratio of azide to lead salt. The product was obtained as a dark-red oil which crystallized as dark-red needles when stored in a desiccator. The crystalline product, stated to be lead(IV) azide, is said to smell like ozone and to decompose spontaneously, sometimes explosively.[82]

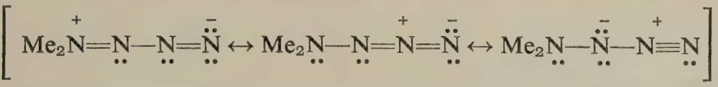
Basic lead azides may be prepared by the hydrolysis of lead azide with water, by the reaction of lead azide with sodium hydroxide, and by precipitation from a solution of a lead salt by a mixture of sodium azide and sodium hydroxide.[83] Products possessing various compositions can be obtained and recent work indicates that the empirical formula for basic lead azide is PbN_6,PbO,nH_2O, where n varies from 0·5 to 1·0; other basic azides have also been described.[84]

The organolead azide, $(C_6H_5)_3PbN_3$, has been prepared by the action of hydrogen azide on the corresponding hydroxide in ethanol–chloroform.[85] It is reported to show no explosive properties.

NITROGEN AND PHOSPHORUS AZIDES

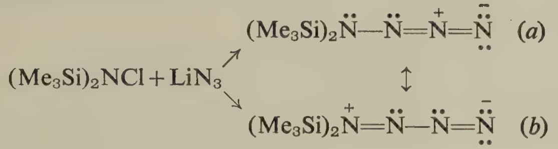
Nitrosyl azide, NON_3, which in earlier references had appeared only as a postulated unstable intermediate in the decomposition of azides by nitrous acid[86–90] and by dinitrogen tetroxide,[86] has been shown to be an unstable yellow compound which decomposes even at −50°.[91] Nitrosyl azide is prepared by several methods, all of which give very low yields (the maximum recorded is 6%). No doubt this is due to the instability of the compound and to the slow and incomplete reactions by which it is formed. The yields in the various methods decreased in the following order of reagents: $NO.HSO_4 + NaN_3 > NO.Cl + NaN_3$ (moist) $> H_2SO_4/HNO_3(1:1) + NaN_3 > HNO_3(70\%) + NaN_3 > HN_3 + NO.HSO_4 > NO.Cl$ (anhydrous) $+ NaN_3$. Although low, the yields from nitrosyl chloride and sodium azide were increased threefold by the addition of water (up to 60 mg. of water per ml. of nitrosyl chloride).

N-Azidodimethylamine, b.p. 32°/11 mm., was obtained in 25% yield by allowing sodium azide and *N*-chlorodimethylamine to react in an inert solvent.[92] This compound, which is explosive, was characterized by the presence of bands at 2110 and 1210 cm.$^{-1}$ in the infra-red, by vapour-phase molecular weight measurement, and by an approximate nitrogen determination. Its formula may be written:



$$\left[\overset{+}{\underset{\cdot\cdot}{\mathrm{Me_2N}}}{=}\underset{\cdot\cdot}{\mathrm{N}}{-}\underset{\cdot\cdot}{\mathrm{N}}{=}\overset{-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{N}}}} \leftrightarrow \underset{\cdot\cdot}{\mathrm{Me_2N}}{-}\underset{\cdot\cdot}{\mathrm{N}}{=}\overset{+}{\mathrm{N}}{=}\overset{-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{N}}}} \leftrightarrow \underset{\cdot\cdot}{\mathrm{Me_2N}}{-}\overset{-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{N}}}}{-}\overset{+}{\mathrm{N}}{\equiv}\underset{\cdot\cdot}{\mathrm{N}}\right]$$

The reaction between lithium azide and *N*-chlorohexamethyldisilazane gives the corresponding *N*-azido compound.[93] The surprising stability of this compound, especially when compared with *N*-azidodimethylamine, is possibly due to mesomerism between the two forms (*a*) and (*b*), with the presence of the trimethylsilyl groups playing a major rôle:


$(\mathrm{Me_3Si})_2\mathrm{NCl} + \mathrm{LiN_3}$
$(\mathrm{Me_3Si})_2\ddot{\mathrm{N}}{-}\ddot{\mathrm{N}}{=}\overset{+}{\mathrm{N}}{=}\overset{-}{\ddot{\mathrm{N}}}$ (*a*)
$(\mathrm{Me_3Si})_2\overset{+}{\mathrm{N}}{=}\ddot{\mathrm{N}}{-}\ddot{\mathrm{N}}{=}\overset{-}{\ddot{\mathrm{N}}}$ (*b*)

N-azidohexamethyldisilazane
or 1:1-bis-(trimethylsilyl)-tetrazdiene.

The structures of the silyl and methyl azides and *iso*cyanates have been discussed and explanations offered to account for the non-linearity of these molecules.[94]

The preparation of the highly explosive compound, P_3N_{21}, by the ready reaction of sodium azide and trimeric phosphonitrile chloride, $(PNCl_2)_3$, in acetone has been reported.[95] The compound, referred to as trimeric phosphonitrile azide, $[PN(N_3)_2]_3$, is a colourless oil insoluble in water, soluble in organic solvents, stable to alkalis but decomposed by concentrated nitric acid, and readily detonated by friction.

Several types of organophosphorus azides have been described. Diarylphosphonyl chlorides react smoothly with sodium azide in anhydrous media, e.g., pyridine, benzene, and acetonitrile, to give the corresponding azides in good yield.[96] For example, an 87.4% yield is obtained in the reaction in which diphenylphosphonyl azide (b.p. 137–140°/0·05 mm.) is prepared:

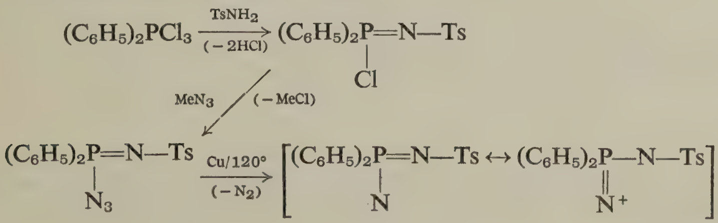
$$(C_6H_5)_2POCl + NaN_3 \rightarrow (C_6H_5)_2PON_3 + NaCl$$

These compounds are quite stable to heat, have strong infra-red absorption at 4·65 μ, and react easily with trivalent phosphorus compounds thus:

$$Ar_2P(O)N_3 + PR_3 \rightarrow Ar_2PON{=}PR_3 + N_2\uparrow$$

Diphenylphosphonyl azide can be used as a simple source of hydrogen azide in organic systems and the liberation of nitrogen in the reaction with trivalent phosphorus compounds can be utilized in the production of stable foamed plastics.[97]

P-Diphenyl-*N*-tosylphosphazen azide, $(C_6H_5)_2PN_3{=}N.Ts$ (Ts = tosyl = toluenesulphonyl), has been obtained by the action of methyl azide on the corresponding chloride, and methyl chloride is eliminated.[98] The azide, m.p. 86°, normally decomposes above 220° but in the presence of copper decomposition occurs at 120° with the loss of one molecule of nitrogen thus:



An azido-derivative of phosphorus(III) is the 'sometimes stable' compound, azido-bis-(perfluoromethyl)-phosphane, $(CF_3)_2PN_3$, which is produced in 70% yield by the interaction of lithium azide and the corresponding chloride at 0° for 24 hr.[99] The azide solidifies, in liquid nitrogen, to a glass, has a vapour-pressure of *ca.* 1 mm./ $-60°$ and *ca.* 57 mm./0° and exhibits a strong band at 4·7 μ in the infra-red.

HALOGEN AZIDES

Details of two methods for the preparation of chlorine azide have been given.[100] In the first, chlorine is passed into a suspension of silver azide in ether at room temperature:

$$AgN_3 + Cl_2 \rightarrow AgCl + ClN_3$$

The preferred method, however, is the addition of acetic acid to an equimolecular mixture of sodium azide and sodium hypochlorite in water. This affords chlorine azide in the reversible reaction:

$$HOCl + HN_3 \rightleftharpoons ClN_3 + H_2O$$

One of the gaseous products from the reaction between fluorine and hydrogen azide, in nitrogen, is said to be fluorine azide (or azine fluoride), which is a greenish-yellow gas, b.p. $-82°$, m.p. $-154°$.[101] The liquid is extremely sensitive to shock and light and usually explodes as it vaporizes. It may be handled at 200 mm.; at this pressure and 25° it decomposes to N_2F_2.

COPPER AND SILVER AZIDES

Copper(I) azide can be obtained by the reduction of copper(II) azide with hydrazine or hydroxylamine,[102] or by the addition of aqueous sodium azide to a reduced copper(II) solution containing a slight excess of reducing agent.[103, 104] Details have been given of the preparation of copper(I) azide by the addition of aqueous sodium azide to a solution of copper(I) chloride in saturated aqueous potassium chloride, containing acetic acid and a trace of potassium bisulphite.[49, 105] Copper(I) azide is precipitated when a copper(II) salt is adsorbed on a Dowex-I–azide ion-exchange resin and reducing agents are added.[106]

Copper(II) azide is readily prepared by the addition of aqueous azide solutions to solutions containing copper(II) ions (Mellor, VIII, 348).[102, 107–110] The compound as commonly obtained is said to contain 0·5–1·0 molecule of water,[107] and various methods have been described for the preparation of the anhydrous material, e.g. by the reaction of copper(II) nitrate trihydrate and lithium azide monohydrate in absolute ethanol,[102] by the decomposition of the complex salt, $Cu(N_3)_2,(NH_3)_2$, at 100–105°,[102] and by the action of aqueous hydrogen azide on fine red copper powder.[102, 107, 108] The last method is said to involve a complex of copper(I) azide with hydrogen azide, oxidation of which by atmospheric oxygen gives copper(II) azide.[102]

Spectrophotometric titration of copper(II) perchlorate by sodium azide in 80:20 (by volume) 2-ethoxyethanol:water indicates the formation of CuN_3^+ and possibly $Cu_2(N_3)_5^-$, $Cu(N_3)_4^{2-}$, and $Cu(N_3)_6^{4-}$ ions.[111] In a study of stability constants pK of CuN_3^+ at an ionic strength of 0·05–0·2 was found to be $-2{\cdot}92$ to $-2{\cdot}99$ at 20°.

Silver azide is prepared by the usual techniques for insoluble azides and laboratory details have been published.[112–5] If silver nitrate and sodium azide are allowed to react in dilute aqueous ammonia then large crystals of silver azide are produced, and the yield is increased from 63 to 93% if the mixture is slowly neutralized with dilute nitric acid.[116] Recrystallization of silver azide from ammonium hydroxide is also recommended for the preparation of large crystals.[49, 114, 117]

CADMIUM AND MERCURY AZIDES

Cadmium azide, $Cd(N_3)_2$, is obtained as a pure, colourless microcrystalline product by the treatment of the impure material with 50% aqueous hydrogen azide.[118] This procedure obviates the formation of the basic azide which normally occurs when the azide is treated with hot water. Contrary to earlier observations on a light yellow product (Curtius and Rissom, 1898. Mellor, VIII, 251) pure cadmium azide is an extremely hazardous substance: it is said to detonate when heated on a metal plate and to explode when rubbed with a horn spatula.[118] The tendency of cadmium azide to hydrolyse has been emphasized and special precautions necessary for its preparation have been given.[119, 120] Thus cadmium carbonate is dissolved in hot aqueous hydrogen azide and 50% aqueous hydrogen azide added; cadmium azide separates on cooling. When solutions of cadmium nitrate and sodium azide are admixed and allowed to stand a precipitate forms. If this is filtered off and the filtrate kept over concentrated sulphuric acid large crystals (*ca.* 1 mm.) of cadmium azide are formed.[121]

Solutions containing cadmium and azide ions in a perchlorate medium, over the range of azide concentrations 0·05–2·00 M. and at an ionic strength of 2·00, have been examined polarographically at 25° ± 0·1°.[122] Use of the analytical method of de Foord and Hume[123] revealed the existence of the following five products:

	CdN_3^+,	$Cd(N_3)_2$,	$Cd(N_3)_3^-$,	$Cd(N_3)_4^{--}$,	$Cd(N_3)_5^{3-}$.
Formation constant	25	400	800	1000	1800

These values, which were confirmed by Leden's method of calculation,[124, 125] were held to reveal the more pronounced tendency of cadmium to form complexes with azide than thiocyanate, demonstrated by the existence of five species compared with four from thiocyanate. The fifth species, which is not common in cadmium complexes, is also demonstrated by calculation of the number of ligands corresponding to the last increment of azide concentration, in the conventional manner from a plot of $E_{1/2}$ against log C. By this means a value of 4·7 ligands is obtained.

Mercury(I) azide is conveniently prepared by the addition of a solution of mercury(I) nitrate, acidified with nitric or acetic acid, to aqueous sodium azide.[49, 126] The preparation must be performed in the dark and the product stored likewise since it rapidly turns orange-yellow when exposed to light.

Complex Azides

BASIC AZIDES

The existence of two basic copper azides has been demonstrated.[107, 108, 127] Further investigation of Wöhler's basic copper azide, $CuO,Cu(N_3)_2$, (Mellor, VIII, 348) has shown that it has the composition $Cu(OH)(N_3)$[127]; it is produced by the action of water at 70–80°,[127] or more slowly of moist air,[107] on copper(II) azide. A second basic copper azide, $Cu(N_3)_2,2Cu(OH)_2$, is produced by the action of water at 80° on the complex, $Cu(NH_3)_2(N_3)_2$.[127]

With transition metals the hydrolysis of azide solutions or the addition of aqueous hydrogen azide to an oxide affords a series of hydroxy-azides.[128] Thus the hydroxy-azides, $M(OH)(N_3)$, where M is Mn, Co, Ni, Cu, and Zn, have been prepared and their structures examined.

When a solution of hydrogen azide in carbon tetrachloride is added dropwise to finely-ground, dry chromium(VI) oxide and phosphorus pentoxide (3:1) at −20° the following reaction takes place[129]:

$$CrO_3 + 2HN_3 \rightarrow CrO_2(N_3)_2 + H_2O$$

If the reaction is accomplished at −70° in dichlorodifluoromethane, followed by evaporation of the solvent and excess of hydrogen azide at very low temperatures, the chromyl azide is obtained as very dark violet crystals which are sensitive to moisture and to light, and explode above 60°.[129] The chromyl azide thus formed has λ_{max} at 459 mμ (ϵ, $3{\cdot}66 \times 10^3$) and 545 mμ (ϵ, $3{\cdot}21 \times 10^3$).

DOUBLE SALTS

The formation of several double salts between mercury(II) cyanide and alkali and alkaline-earth metal azides has been described together with their crystallographic data.[130] The salts, $Hg(CN)_2$, M^IN_3, xH_2O or $Hg(CN)_2$, $M^{II}(N_3)_2$, xH_2O, are either monoclinic when $M^I = Li$, NH_4, Na, or orthorhombic when $M^I = K$ or $M^{II} = Ca$, Sr, Ba. Detailed comparisons of the preparation and properties of the double salts of mercury(II) cyanide with the alkali halides and azides have been made.[131]

The crystalline compounds formed by the addition of aqueous sodium azide to solutions of thallium acetate, lead acetate, ammoniacal mercury(II) sulphate, and ammoniacal silver nitrate have been described.[132]

Double salt formation has been observed in the systems lead azide–lead chloride, and lead azide–lead bromide.[133] Each double salt contained about 50% of the respective halide.

CO-ORDINATION COMPOUNDS

The long-continued study of the close similarity of the azide with the halide ion has prompted several investigations into the preparation of complex azido-ammines. The result of one of these investigations was the preparation of the following[134]: (py = C_5H_5N, en = $H_2NCH_2CH_2NH_2$)

$[Cr(NH_3)_6](N_3)_2$, $[Cr(NH_3)_5Cl](N_3)_2$; $[Ni(NH_3)_2](N_3)_2$, $[Ni(NH_3)_6](N_3)_2$,
$[Ni\ py_2](N_3)_2$, $[Ni\ py_6](N_3)_2$, $[Ni\ en_3](N_3)_2$; $[Cu(NH_3)_2](N_3)_2$, $[Cu(NH_3)_4](N_3)_2$,
$[Cu\ py_2](N_3)_2$, $[Cu\ en_2](N_3)_2$; $[Zn\ py_2](N_3)_2$, $[Zn\ en_3](N_3)_2$; $[Cd\ py_2](N_3)_2$,
$[Cd\ en_2](N_3)_2$; $[Hg\ py](N_3)_2$.

It was not found possible to prepare analogous silver and thallium salts.

The complex compounds formed from copper(II) azide have been the subject of extensive investigations.[135–140] Three types of complex have been distinguished[135]:

1. Penetration complexes.
2. Non-electrolytes.
3. Binuclear complexes and addition compounds.

The co-ordination numbers of these three types are (1) 4, 2, (2) 4, 3, (3) 6, 4, and 3.

Compounds of type (1) were prepared by the following methods:

(*a*) From copper(I) or copper(II) azide and an amine in alcoholic solution.
(*b*) From copper(II) salts and sodium azide in a methanolic solution of an amine.
(*c*) From copper(II) azide and soluble amine salts.
(*d*) By boiling methanolic solutions of highly amminated compounds to give simpler compounds.

The following penetration complexes were thus obtained: $[Cu(NH_3)_4](N_3)_2$, $[Cu(CH_3NH_2)_4](N_3)_2$, $[Cu\ en_2](N_3)_2$, and $[Cu\ pn_2](N_3)_2$.

The following compounds were classed as non-electrolytes because of their low solubility, low electrical conductivity, stability towards water, green-brown colour, and because the azide ion is probably smaller than the ammonia molecule (pn = propylenediamine, en = ethylenediamine, py = pyridine)[136]:

$[(N_3)_2Cu(R{\cdot}NH_2)_2]$, where R = H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, *iso*-C_4H_9, C_6H_5, p-$Cl{\cdot}C_6H_4$, p-$Br{\cdot}C_6H_4$; $[(N_3)_2Cu\ en]$, $[(N_3)_2Cu\ pn]$, $[(N_3)_2Cu\ py_2]$, $[(N_3)_2Cu\ py]$, $[(N_3)_2Cu(H_2N{\cdot}CH_2CH_2OH)Cu(N_3)_2]$.

These compounds were obtained in the following ways:

(*a*) When copper(II) azide is dissolved in an amine solution a blue solution is formed which is an equilibrium mixture of the penetration complex and the non-electrolyte. If the amine concentration is lowered by the addition of acid, methanol, ether, etc., then the equilibrium is disturbed and the non-electrolyte is precipitated.

(*b*) The non-electrolyte complexes are precipitated when sodium azide is added to a solution of a copper(II) salt in an amine.

(*c*) Addition complexes or 'cuprates' of aliphatic amines rearrange to the non-electrolyte form.

By these methods a large number of complex compounds were obtained from almost all the common complex-forming organic bases including several alkaloids.[137] These compounds were of the following types:

(i) $[(N_3)_2Cu(base)_2]$, thirteen compounds, mostly green in colour.
(ii) $[(N_3)_2Cu(base)]$, eighteen compounds, brown to dark-green.
(iii) $[(N_3)_2Cu(base)Cu(N_3)_2]$, six compounds, brownish green.

Most of the compounds have the co-ordination number 3, while 4 was not exceeded. When the co-ordination number is decreased, i.e., in compounds of copper(I), the colour changes to white. The explosive force of these compounds, which is independent of the azide-nitrogen content, decreases in the order (i) > (ii) > (iii).

Copper(II) azide dissolves in aqueous or alcoholic solutions of soluble azides to form addition compounds or 'cuprates' in which copper is anionic[138, 139]:

(iv) $[Cu(N_3)_6]^{4-}$
(v) $[Cu(N_3)_4]^{2-}$
(vi) $[Cu(N_3)_3]^-$
(vii) $[(N_3)_2CuN_3Cu(N_3)_2]^-$

Compounds of types (iv) and (v) are stable only in concentrated aqueous solution, (vi) only in alcoholic solution, and (vii) only in the presence of an excess of the amine azide or hydrogen azide. These cuprates cannot always be prepared by dissolution of copper(II) azide in the amine azide since in many cases rearrangement to complexes of the penetration or non-electrolyte (i–iii) type occurs. Each time such a solution is made, however, an opaque dark red-brown colour is produced and the products are usually isolated as red-brown or brown, occasionally greenish and red violet, needles. The precipitation of the black copper(II) azide on dilution with water serves to distinguish the cuprates from the penetration complexes and the non-electrolytes; the water-soluble cuprates are of course good conductors of electricity, e.g., due to the equilibria:

$$\text{Amine H}[Cu(N_3)_3] \rightleftharpoons \text{Amine H}^+ + [Cu(N_3)_3]^- \rightleftharpoons \text{Amine H}^+ + N_3^- + Cu(N_3)_2$$

The following cuprates have been described:

Type (iv): Lithium, which crystallizes as the trihydrate; the anhydrous salt is produced by heating the hydrate to 120°.

Type (v): Barium, bis-(dimethylammonium), bis-(*n*-butylammonium), bis-(*iso*-butylammonium), dipiperidinium, bis-(*cyclo*hexylammonium).

Type (vi): Sodium, ammonium, tetramethylammonium, *iso*butylammonium, piperidinium, benzylammonium. Also of type (vi) are the following diazidohalogenocuprates and azidodihalogenocuprates: piperidinium diazidochlorocuprate; methylammonium, ethylammonium, and dimethylammonium diazidochloro (and bromo)cuprates; dimethylammonium azidodichloro (and dibromo) cuprate; dimethyl- and diethyl-ammonium diazidonitratocuprate. The last two compounds are best prepared from the amine azide and copper(II) nitrate.

Type (vii): Penta-azidodicuprates have been prepared with the following bases providing the cation: dimethylamine, diethylamine, trimethylamine, *ortho-* and *meta*-chloraniline, *N*-methylaniline, *N, N*-dimethylaniline, *N, N*-diethylaniline, *vic-meta*-xylidine, pyrrole, quinaldine, and 8-methylquinoline. Also belonging to type (vii) is mono-ethanolammonium tetrazidochlorodicuprate.

The compound 'copper azide chloride', $Cu(N_3)_2,3CuCl_2$ has been described.[138] It is normally obtained as a hexahydrate which cannot be dehydrated, but the anhydrous compound can be prepared using absolute alcoholic solutions.

The preparation of azidocuprates from the elements of the first and second groups of the periodic table has been studied.[140] The following compounds were obtained and studied: potassium triazidocuprate, rubidium penta-azidodicuprate, cæsium penta-azidodicuprate, and strontium tetra-azidocuprate. Although calcium azide dissolved in the copper(II) azide solution with the formation of the characteristic red-brown cuprate colour it was not found possible to isolate such a product. The solubility properties did not permit azidocuprates to be prepared from beryllium, magnesium, silver, gold, zinc, cadmium, and mercury. The stability towards water and the ease of crystallization of the compounds obtained increased with the atomic weight of the cation, while the solubility in water decreased.

A wide range of azido-ammine complexes of cobalt has been studied and two clearly distinguishable types have emerged. Thus, the azide groups are either closely associated with a particular cobalt atom, the bond displaying some covalent properties, or shielded from the cobalt atom by the ligand sphere.[141] The first type, e.g., $[Co(NH_3)_3(N_3)_3]$, are non-electrolytes and have the asymmetric character of covalent azides such as hydrogen azide, methyl azide etc. The second type, e.g., $[Co(NH_3)_6](N_3)_3$, are ionic and symmetrical as in simple salts such as sodium azide.

The azide entity can be introduced into the co-ordination sphere of cobalt(III) either by substitution of azide for water[142–4] or chlorine,[145] or by synthesis from a cobalt(II) salt and the other constituents followed by aerial oxidation.[142, 144, 145] For example:

	Reference
$[Co(NH_3)_5H_2O]^{3+} \rightarrow [Co(NH_3)_5N_3]^{3+}$	142
$[Co(NH_3)_4(H_2O)_2]Cl \rightarrow$ *cis*- and *trans*-$[Co(NH_3)_4(N_3)_2]N_3$	143
$[Co(NH_3)_4H_2O]^{3+} \rightarrow [Co(NH_3)_3(N_3)_3]$	144
trans-$[Co\ en_2Cl_2]^+ \rightarrow$ *cis*- and *trans*-$[Co\ en_2(N_3)Cl]^+$	145
cis- and *trans*-$[Co\ en_2(N_3)Cl]^+ \rightarrow$ *cis*- and *trans*-$[Co\ en_2(N_3)_2]^+$	145
$Co^{++} + N_3^- + NH_3 + NH_4^+ \xrightarrow{[O]} [Co(NH_3)_5N_3]^{++}$	142
$Co^{++} + N_3^- + NH_3 + NH_4^+ \xrightarrow{[O]} [Co(NH_3)_3(N_3)_3]$	144
$Co(NO_3)_2,6H_2O + NaN_3 + H_2O +$ ethylenediamine (en) $+ HNO_3$ $\xrightarrow{[O]}$ *cis*-$[Co\ en_2(N_3)_2]NO_3$	145

By making use of the different solubilities of the various salts in the series, double decomposition between appropriate reactants affords complexes with a wide range of anions. Thus the preparation of the following has been described:

(*a*) $[Co(NH_3)_5N_3]X_2$, where $X = Cl^-, Br^-, I^-, N_3^-, NO_3^-, \frac{1}{2}S_2O_3^{--}, \frac{1}{2}S_2O_6^{--}, \frac{1}{2}HgCl_4^{--}, \frac{1}{2}HgI_4^{--}$, and $\frac{1}{2}CrO_4^{--}$.[142]

(*b*) *cis*- and *trans*-$[Co(NH_3)_4(N_3)_2]X$, where $X = Cl^-, Br^-, I^-, N_3^-, NO_3^-$ and ClO_4^-.[143] In this series it was not found possible to substantiate the previously claimed[146] *cis–trans* interconversion.

(*c*) *cis*-$[Co\ en_2(N_3)_2]X$, where $X = Br^-, I^-, N_3^-, CNS^-, \frac{1}{2}S_2O_6^{--}$, and ClO_4^-.[145] The *cis*-bromide was also converted to the (+)-*cis*-antimonyl-(+)-tartrate.

Hexamminecobalt(III) perchlorate, prepared from the corresponding chloride, when treated in formdimethylamide with sodium azide gives the double salt: $[Co(NH_3)_6](N_3)_3,3NaN_3$.[147] When this double salt is recrystallized from water at 60–70° the solid product obtained is hexamminecobalt(III) azide, $[Co(NH_3)_6](N_3)_3$.

Spectrophotometric investigation of solutions containing cobalt(II) and azide ions indicated the presence of the ion CoN_3^+ in solution.[148] If the aqueous solution contains a large excess of azide ions then the ion $Co(N_3)_4^{--}$ could be isolated as its tetraphenylphosphonium and tetraphenylarsonium salts. The blue colour produced when water-miscible alcohols, dioxan, or acetone is added to the pink-violet Co^{++}–N_3^- solution is attributed to the $Co(N_3)_4^{--}$ ion.

Complex compounds analogous to those derived from cobalt have been prepared from chromium. Thus *cis*-dichloro-bis-(ethylenediamine)chromium(III) azide, *cis*-$[Cr\,en_2Cl_2](N_3)$, and hexa-ethylenediaminehexahydroxochromium hexa-azide $[Cr_4(OH)_6\,en_6](N_3)_6$, have been prepared as their pentahydrates.[149] A series of compounds has been prepared with the azido group as part of the co-ordination sphere of the chromium:

(*a*)[150]

$$\begin{array}{c} [Cr\,en_3]Cl_3 \\ \text{excess}\ \Big\downarrow\ NaN_3 \\ cis\text{-}[Cr\,en_2(N_3)_2](Cl,N_3) \\ \Big\downarrow \\ cis\text{-}[Cr\,en_2(N_3)_2]X \\ (\text{where } X = N_3^-,\ Br^-,\ I^-,\ ClO_4^-,\ NO_3^-) \end{array}$$

(*b*)[151]

$$\begin{array}{c} \underbrace{[Cr(NH_3)_5H_2O](ClO_4)_3,\ NaN_3,\ NaX,\ CH_3{\cdot}COOH} \\ \Big\downarrow \\ [Cr(NH_3)_5N_3]X_2 \\ (\text{where } X = Cl^-,\ Br^-,\ I^-,\ ClO_4^-,\ NO_3^-) \end{array}$$

(*c*)[151]

$$\begin{array}{c} [Cr(NH_3)_6]Cl_3 \\ \Big\downarrow\ NaN_3,(NH_4)_2SO_4 \\ [Cr(NH_3)_3(N_3)_3] \\ (80\%\ \text{yield}) \end{array}$$

The intense green colour produced when solutions of chromium(III) nitrate and sodium azide are admixed has been attributed to a 1:1 complex chromium(III) monoazide compound.[151a] (λ_{max}: 4420, 6050 A.). Excess of azide ion causes the solution to turn deep blue (λ_{max}: 4800, 6500 A.) and it was stated that the green solution contains positively charged complexes whereas the blue solution contains negatively charged complexes. The instability constant determined by the molar ratio method as 0·0214[151a] has been held to be in error due to neglect of the basicity of sodium azide and hydrolysis of this is said to be responsible for inconsistencies in the earlier treatment.[151b]

The blood-red colour which is produced when solutions containing azide and ferric ions are admixed has long been known (Mellor, VIII, 342, 354), but the nature of the entity responsible for the colour was not clearly understood and further investigations have been made. Solutions containing ferric chloride and azide ions, in the presence of hydrochloric acid, have been studied spectrophotometrically and the results interpreted in the light of an aquo complex such as $[Fe(H_2O)_5N_3]^{++}$.[152] The intensity of the colour produced increases as the azide:ferric ratio increases. This indicates that the complex is highly dissociated.[153] Up to a molar ratio of twelve a mean value of $8{\cdot}62 \times 10^{-3}$ is obtained for the equilibrium constant for the formation of the complex; at higher molar ratios complexes containing more than one co-ordinated azide group may be present. The blood-red colour has also been ascribed to the complex ion $[FeN_3]^{++}$, and it has been suggested that ferric azide has the structure, $[FeN_3](N_3)_2$.[154] The second-order rate constant for exchange between aquated Fe^{++} and the $[FeN_3]^{++}$ complex has been determined as 1800 l. mole^{-1}sec.$^{-1}$ at 0°.[155] It has been stated that conductimetric and cryoscopic measurements show that in the reaction between 0·015 M. ferric chloride and sodium azide no iron azides are formed but that the reaction is[156]:

$$FeCl_3 + 3NaN_3 + 3H_2O \rightarrow Fe(OH)_3 + 3NaCl + 3HN_3$$

The purple colour which amminecyanoferrates(II) form with azide ions, and which has been suggested as the basis of a 'spot-test' suitable for identification purposes,[157] has been asserted to be due to aquopentacyanoferrate(III).[158] However, further investigations, which also led to the development of a colorimetric method for the determination of aquo- and ammono-pentacyanoferrate(II), pointed to the formation of a distinct azide complex.[159] This complex has been shown to be azidopentacyanoferrate(III) and the tetrabutylammonium salt, $[Fe(CN)_5N_3](Bu_4N)_3$, has been prepared and analysed.[160]

A complex sodium gold azide, the analytical figures of which correspond most closely to the empirical formula, $NaAu_{1\cdot43}N_{9\cdot05}$, has been prepared as follows[161]:

Hydrogen tetrachloro-aurate(III) was dissolved in dilute hydrochloric acid and the solution extracted with ether. The ether extract was treated with dry crystalline sodium azide whereupon the bright yellow colour rapidly changed to dark red-brown; after a few hours the solution was transferred to fresh sodium azide and the mixture was allowed to stand overnight. Filtration and evaporation to dryness gave the product as orange-red needles, only slightly soluble in dry ether but extremely soluble in water, ethanol, and acetone from any of which it can be recrystallized unchanged.

PHYSICAL PROPERTIES

Ammonium and Alkali and Alkaline-Earth Metal Azides

PHASE EQUILIBRIA AND SOLUBILITY

The phase diagrams for the systems water–lithium azide,[162] water–sodium azide,[163] and water–potassium azide[163] have been described. Lithium azide forms a monohydrate which is deposited from solutions from 68·2 to −31°, and from which it is difficult to obtain the anhydrous salt. From −31° to the eutectic point, −47·5°, there is imperfect deposition of a tetrahydrate and the solutions easily become supersaturated and remain so even when inoculated. The water–sodium azide system has a eutectic point at −15·1° (21·6% NaN_3), and crystals of a trihydrate have been isolated. A saturated aqueous solution of sodium azide contains 28% NaN_3 at 0° and 35·6% at 100°. In the case of the water–potassium azide system the eutectic point is at −12·9°, (26·2% KN_3), and no hydrate is formed. The solubility of potassium azide is 29·3% w/v at 0° and 51·4% w/v at 100°. Experiments with gelatin place sodium azide between the bromide and nitrate in the lyotropic series.[164] From the lyotropic number the heat of hydration was calculated as 71 kcal. mole^{-1}, and the electron affinity as 54 kcal. mole^{-1}, or 2·3 eV. Sodium azide has a solubility which is less than 0·005% w/v at 25° in acetone, chloroform, hexane, *cyclo*hexane, carbon tetrachloride, trichloroethylene, and ethyl acetate.[165] In methanol, sodium azide has a solubility of 2·48% w/v or 3·16 w/w at 25°; and a saturated methanolic solution has a density of 0·8083 g./ml. The solubility of sodium azide in liquid ammonia has been determined from 0° to 42°; it decreases rapidly below −27·3°.[166] It has been found that the solubility of sodamide in liquid ammonia is increased 20 to 30-fold by the addition of increasing amounts of sodium azide.

DENSITY AND OPTICAL PROPERTIES

The density of sodium azide at 25° is given as 1·8473 ± 0·0004 g./ml.[167] The densities of rubidium and cæsium azides are 2·788[32] and 4·65 g./ml.[168] respectively. Other determinations of the densities, refractive indices, and molar refraction of crystalline sodium and potassium azides have been made.[169, 170]

The ultra-violet absorption spectra of aqueous solutions of the azides of lithium, sodium, and potassium have been recorded.[199–202] When the absorption cell is placed between the monochromator and the source, as is usual, the results are said to differ from those obtained when photoelectric counters are used. This difference is attributed to a photochemical activation or predissociation[199] (see page 49).

ELECTRICAL PROPERTIES

The ionic conductances of some alkali and alkaline-earth metal azides have been found to obey the equation[171]:

$$\log \kappa = \log A - \frac{E}{2{\cdot}303RT}$$

The results are summarized in Table I:

Table I.—Ionic Conductance Constants for Azides

Compound	Temperature range (°K)	log *A*	*E* (kcal. mole^{-1})
LiN_3	300–370	0·840	19·1
NaN_3	375–490	0·490	25·0
KN_3	390–500	4·59	30·1
$Ca(N_3)_2$	290–370	−9·56	5·3
$Sr(N_3)_2$	300–380	−10·70	5·1
$Ba(N_3)_2$	295–380	−5·99	11·6

The low activation energy for the structure-sensitive conductance in the potassium, calcium, and strontium azides was stated to be associated with the mobility of surface lattice defects.

The electrical conductivity both of sodium azide in the concentration interval 0·001–1·0 N. and of mixtures of sodium azide and potassium chloride has been studied.[172] The data obtained were used in a study of the additivity of specific conductivity.

DISSOCIATION

The ionization constant of sodium azide at several ionic strengths has been determined by spectroscopic measurements at 220–310 mμ, and the thermodynamic ionization constant has been calculated as $2{\cdot}39 \times 10^{-5}$ mole/l.[173] The products of the activity coefficients of the hydrogen ion and the azide ion at various ionic strengths were compared with Kielland's values.[173]

MOLECULAR AND CRYSTAL STRUCTURE

The linear symmetrical structure of the azide ion in metallic azides is now firmly established.[174] However, the nature of these compounds is by no means completely ionic and, in fact, decreases as the ionization potential of the metal increases.[114]

In sodium and potassium azides each of the end nitrogen atoms is $1{\cdot}150 \pm 0{\cdot}016$ A. and $1{\cdot}145 \pm 0{\cdot}017$ A. from the central nitrogen atom respectively.[175] The greater figure of $1{\cdot}165 \pm 0{\cdot}021$ A. was found for ammonium azide and was attributed to the hydrogen bonding of each terminal nitrogen atom to its two nearest neighbours. The energy of the hydrogen bonds (i.e., N—H····N) in ammonium azide has been given as 4·5 g.-cal. each.[168]

In spite of the overwhelming evidence to the contrary, claims have been made for the asymmetric nature of the azide ion.[176, 177] The results were said to be in agreement with earlier work, but this was concerned with the covalent azides, methyl azide[178] and cyanuric triazide.[179]

Molecular orbital calculations indicate that the charges on the nitrogen atoms of the azide ion are: −0·83, 0·66, and −0·83, respectively, and these atoms are equidistant at 1·16 A.[180] A simplified molecular orbital treatment also predicted a bond length of 1·16 A. but gave a low value for the dipole moment.[181]

The following measurements were made on crystals of sodium and potassium azide prepared as described earlier[27]; the results are in good agreement with the earlier figures[174]:

	Sodium Azide	Potassium Azide
	Rhombohedral	*Tetragonal*
	$a = 5{\cdot}488$ A.	$a = 6{\cdot}091$ A.
	$\alpha = 38°43'$	$c = 7{\cdot}056$ A.
Refractive Index	$n_o = 1{\cdot}38$	$n_o = 1{\cdot}66$
	$n_e = 1{\cdot}52$	$n_e = 1{\cdot}45$

Use of a Geiger counter *X*-ray diffractometer, employing CuK_α radiation, has enabled the diffraction data of potassium azide and potassium cyanate to be determined in a more quantitative manner.[182] It was shown that the lattice parameters of these two compounds are nearly identical and that the pseudo-cæsium chloride type lattice of potassium azide is also possessed by KO_3.

Rubidium and cæsium azides are similar to potassium azide in structure, i.e., body-centred tetragonal and have four molecules per unit cell.[32, 183–5] The cell constants are a, $c = 4{\cdot}497$, $3{\cdot}707$,[32] and $6{\cdot}36$, $7{\cdot}41$[186] respectively.

It has been observed that the increasing ionic radius of alkali-metal ion results in an increase in a and c and that a value of 1·63 A. for the contact radius of the azide group (end atom) satisfies the metal atom–end nitrogen atom distance in potassium, rubidium, and cæsium azides.[2, 114] The hexagonal structure of sodium azide is attributed to the smaller ionic radius of sodium[2]; this change in structure has also been explained in terms of the azide ion being an ellipsoid of revolution.[187]

Powder photographs of sodium azide, at 25° and 200°, show a marked anisotropy of thermal expansion.[188] The cell dimensions at these temperatures were found to be $a = 3{\cdot}62$ and $3{\cdot}67$, $c = 15{\cdot}13$ and $15{\cdot}10$ A.

The structure of the azide ion has been extensively studied by infra-red absorption and Raman spectra.[189–194] The principal absorption regions are near 645 (bending frequency), 1350 (symmetrical stretching frequency), and 2070 cm.$^{-1}$ (asymmetrical stretching frequency). The observed frequencies varied only slightly with the cation, thus indicating that, in this connection, the variations in polarizing power and ionization potential are of little importance in this series.

Some inorganic azides were included in a study of the infra-red absorption spectra of inorganic ions in the cæsium bromide region (700–300 cm.$^{-1}$).[195] The azide ion was also included in a study of polyatomic ions isolated in alkali halide lattices; spectra were obtained over the range 5–500°K.[196]

Ammonium azide has been examined in detail by infra-red spectroscopy.[3, 197] At 68°K. the solid, sublimed on to a cold salt window, appears to be a disordered crystal which becomes ordered when it is warmed above 150°K.; a detailed vibrational assignment was made. The absorption spectra of the solid produced when the glow-discharge decomposition fragments of hydrogen azide were condensed on a surface at 90°K. at several temperatures were interpreted as involving HN_3, NH_4N_3, NH_3, N_2H_2, and $(NH)_x$. The spectrum of ammonium azide in the form of a mull has also been recorded[194]: 1345 (ν_1 = symm. stretching), 661 and 650 (ν_2, bending), and 2041 (ν_3, asymm. stretching). The splitting of the bending frequency, ν_2, was attributed to hydrogen bonding. A detailed study has been made of the infra-red absorption spectra, structure, and hydrogen-bonding in a series of ammonium salts which included the azide.[198] These exhibited a combination frequency, $\nu_4 + \nu_6$, involving a torsional mode, and a multiplicity of lines at 3000 cm.$^{-1}$ All the salts studied differed in structure from the corresponding potassium and rubidium salts and it was concluded that the ammonium ion is locked in position in the crystal lattice by hydrogen-bonding. When ammonium azide, prepared as previously described,[1] is recrystallized from ethanol and dried *in vacuo*, it is orthorhombic, unlike the potassium and rubidium salts which are tetragonal, and the following assignments were made: $\nu_4 = 1414$, $\nu_4 + \nu_6 = 1810$, $2\nu_4 = 2830$, $\nu_2 + \nu_4 = 3000$, $\nu_3 = 3140$, and the torsional oscillation $\nu_6 = 396$ cm.$^{-1}$. The bands observed at 1441, 1428, and 1420 cm.$^{-1}$ at 69°K. were replaced by one band at 1415 cm.$^{-1}$ at room temperature.

The structure of strontium azide has been completely determined by means of three-dimensional Fourier sections and lines using single-crystal rotation photographs with Cu-K_α *X*-rays.[203] The lattice is orthorhombic, of space group *Fddd*, and has the dimensions $a=11{\cdot}82$, $b=11{\cdot}47$, and $c=6{\cdot}08$ A., with eight molecules in each unit cell. The bond distances are: N—N, 1·12; Sr—N_1, 2·63; Sr—N_2, 2·77 A.; each of these two strontium–nitrogen distances is associated with four nitrogen atoms. The larger figure of 2·77 A. corresponds to ionic bonding (ionic radius of strontium = 1·13 A., and of azide ion = 1·63 A.) whilst the lower figure may point to some form of directed bonding.

Other physical properties of sodium, silver, thallium and barium azides are referred to later (see page 43).

Other Divalent Metal Azides

The structural investigations of the other divalent metal azides have been restricted to the determination of cell dimensions and the number of molecules per unit cell. Thus copper(II),[102] calcium,[2] and cadmium[204] azides are orthorhombic and have eight molecules per unit cell; the cell dimensions are, respectively, a, b, $c=9{\cdot}23$, 13·23, 3·07; 11·62, 10·92, 5·66; 7·82, 6·46, 16·04 A. The density of cadmium azide is 3·24 (in benzene at 20°) whilst the calculated figure is 3·20 ± 0·04 g./ml.[204]

α-Lead azide[205–8] is orthorhombic and has twelve molecules in the unit cell, whereas β-lead azide[206–8] is monoclinic and has eight molecules in each unit cell. The details given in Table II have been published for these two polymorphs.[207]

Table II.—Physical Properties of Lead Azide

	α-Lead Azide[207]	β-Lead Azide[207]
Crystal Morphology	orthorhombic	monoclinic
$a:b:c$	0·700:1:0·408	2·063:1:0·577 $\beta=107{\cdot}5°$ (107° 35′[206], 90° 49′[205])
X-ray Space Group	$Pc2_1n$ or $Pcmn$	Cm, $C2$ or $C2/m$
a	11·41 (11·31[206], 11·312[205])	18·31 (18·49[206], 17·508[205])
b	16·31 (16·25[206], 16·246[205])	8·88 (8·84[206], 8·844[205])
c	6·66 (6·63[206], 6·628[205])	5·12 (5·12[206], 5·090[205])
Formula weights per unit cell	12 (12·07 calculated from *X*-ray)	8 (8·10 calc.)
Formula weight	291·3	291·3
Density	4·68 (*X*-ray) 4·71 (benzene[79]) 4·716 (ether, 15°[209])	4·87 (*X*-ray) 4·93 (ethylene dibromide[89])
Refractive Index (5893 A., 25°)		
α	1·86 ± 0·01	1·98 ± 0·03
β	2·24 ± 0·01	2·14 ± 0·01
γ	2·64 ± 0·01	2·7 (Calc. from α, β, 2V)
Optical Axial Angle $2V$	76·6 (calc. from α, β, γ)	67° ± 3 (estimated from curvature of the brushes)
Molecular Refraction (5893 A., 25°)	$\sqrt[3]{\alpha\beta\gamma}=2{\cdot}22$ *R*(obs.) = 35·1	$\sqrt[3]{\alpha\beta\gamma}=2{\cdot}26$ *R*(*obs*) 34·7

Other physical properties of lead azide are referred to later (see page 45).

Barium azide forms monoclinic-prismatic or holohedral crystals, space group C_{2h}^{1} or C_{2h}^{2}, which have ten molecules per unit cell, a, b, $c=6{\cdot}22$, 29·29, 7·02 A., $\beta=105°\ 14'$, from which a density of 2·937 has been calculated.[32]

Other Monovalent Metal Azides

STRUCTURE

Thallium(I) azide forms pale yellow needles, m.p. 334°, which are isomorphous with the azides of potassium and rubidium.[2, 210]. The crystals are tetragonal with four molecules per unit cell; a, $c = 6{\cdot}23$, $6{\cdot}88$ A.[114]; other values which have been given are a, $c = 6{\cdot}21$, $7{\cdot}37$ A.[211]

Silver azide forms orthorhombic crystals with four molecules per unit cell, a, b, $c = 5{\cdot}93$, $5{\cdot}58$, $6{\cdot}04$ A.[212] The calculated density is 4·81 and the N—N bond length is 1·18 A.[212]; the observed density, in benzene at 15°, is 5·1.[209] The above figures give the ratio $a{:}b{:}c = 1{\cdot}065{:}1{:}1{\cdot}082$; the ratios $1{\cdot}053{:}1{:}1{\cdot}072$,[213] and $1{\cdot}055{:}1{:}1{\cdot}068$[211] have also been given.

Copper(I) azide forms colourless tetragonal crystals. Specimens suitable for crystal analysis can be obtained by saturating, at 65°, with dry copper(I) azide a hot saturated solution of potassium chloride, containing 0·1% potassium bisulphite; the solution is filtered and the filtrate allowed to cool slowly.[49, 105] Unlike the other monovalent azides, copper(I) azide has eight molecules per unit cell, the constants for which are: $a = 8{\cdot}65$, $c = 5{\cdot}59$ A.[104]; the N—N distance is 1·12 A. The calculated density is 3·34 g./ml., whilst the observed value is 3·26 g./ml. The structure, which is not related to any known standard type, consists of copper ions and azide ions arranged in chains in the direction of the body-diagonal of the cell.

SOLUBILITY AND IONIC EQUILIBRIA

The solubility products of silver, thallium(I), mercury(I), and lead azide have been determined by the measurement of the electromotive force of appropriate cells[214–5]:

$$K_{s\mathrm{AgN_3}} = 2{\cdot}88 \times 10^{-9}\ (25°). \qquad K_{s\mathrm{Hg_2N_6}} = 7{\cdot}00 \times 10^{-10}$$
$$K_{s\mathrm{TlN_3}} = 2{\cdot}19 \times 10^{-4}. \qquad K_{s\mathrm{PbN_6}} = 2{\cdot}58 \times 10^{-9}$$

By means of a differential potentiometric microtitration $K_{s\mathrm{AgN_3}}$ was determined as $1{\cdot}6 \pm 0{\cdot}2 \times 10^{-9}$, in 4 M. sodium perchlorate.[216] This investigation showed that no polynuclear complexes carrying the charges +1, −2 or −3 existed, but that the following probably did so: AgN_3, $Ag(N_3)_2^-$, $Ag(N_3)_3^{--}$, and $Ag(N_3)_4^{---}$; of these, $Ag(N_3)_2^-$ is more stable than the others. The solubility of silver azide in water has been calculated to be $5{\cdot}1 \times 10^{-5}$ mol./l. at 25°[217]; it has also been quoted as $3{\cdot}9 \times 10^{-5}$ mol./l. at 17°,[218] and $9{\cdot}07 \times 10^{-5}$ mol./l.[219] In 0·005 N. sodium azide the solubility is said to fall to about one tenth of the value in water.[218]

Silver azide readily dissolves in a mixture of equal volumes of monoethanolamine and ammonium hydroxide and is precipitated in a finely-divided condition by the addition of dilute acetic acid.[220] Lead azide behaves similarly but there is a loss of explosive properties on reprecipitation. Di- and tri-ethanolamines are less efficient solvents than monoethanolamine.

The molal b.p. rise of solutions of silver azide in hydrogen fluoride indicates the formation of four ions per mole, with the possible production of $AgFH^+$, HN_3H^+, and $2F^-$.[221] In comparison, mercury(II) azide gives three ions per mole with the possible production of $HgN_6H_2^+$ and $2F^-$, and lead azide reacts with hydrogen fluoride with the liberation of gaseous hydrogen azide and the precipitation of lead fluoride.

Hydroxy-azides

The structures of some hydroxy-azides, $M(OH)N_3$, have been examined.[128] Where M = Co and Zn the metal atoms are situated above one another, with the azide and hydroxide groups forming alternate horizontal layers. Manganese hydroxyazide has a $C19$ structure as have the compounds $Zn(OH)_{2-x}(N_3)_x$, where $x = 0{\cdot}9$ to $0{\cdot}67$, with the hydroxide and azide groups statistically distributed. In the compound $Zn_4(OH)_8,Zn_2(N_3)_2$, three of the zinc atoms are octahedral and two are tetrahedral; the compound belongs to the space group $C_{2h}^3 - C2/m$ and the unit cell has the dimensions: $a = 9{\cdot}98$, $b = 6{\cdot}28$, $c = 9{\cdot}54$, and $c \sin\beta = 9{\cdot}19$A.

CHEMICAL PROPERTIES

Special Reactions

AMMONIUM AZIDE

Ammonium azide, when heated for twenty hours in benzene at 260–280°, or xylene at 250–60°, decomposes to 'NH_3N_2' together with a 'black humus'.[222]

SODIUM AZIDE

When sodium azide is heated *in vacuo* at 537°K., and simultaneously irradiated with a mercury lamp, the white sample turns purple and a temperature-stable optical absorption band, attributed to colloidal sodium, is formed.[223] The electrolysis of aqueous sodium azide produces nitrogen and hydrogen at the anode and cathode respectively, in the volumetric ratio 3:1.[224] The addition of resorcinol or hydroquinone reduces this ratio to 0·73 to 0·90:1 and 0·48 to 0·55:1, respectively. Dissolution of sodium azide in anhydrous hydrogen fluoride leads to decomposition of the azide with evolution of hydrogen azide.[225] In the ozonolysis of aqueous sodium azide there is produced initially a yellow colour which deepens to orange-red after several hours.[226] The colour of the solution is discharged by: (i) further ozonolysis, (ii) allowing the solution to stand for some time, (iii) acids, and (iv) reducing agents. The stability of the colour is increased by the addition of alkali. Although it has not proved possible to isolate the substance responsible for the colour it has been suggested that it is a sodium salt of an acidic derivative of hydrogen peroxide, such as pernitrous acid, formed by the decomposition of an ozonide of hydrogen azide, thus:

$$HN_3 + O_3 \rightarrow HN_3(O_3) \rightarrow HO{-}O{-}NO + N_2$$

Sodium azide is reduced, in the presence of colloidal palladium, in accordance with the equation[227]:

$$NaN_3 + H_2 \rightarrow NaNH_2 + H_2$$

No reaction was observed when the hydrogen was replaced by carbon dioxide. The reduction of sodium azide by aluminium amalgam gives ammonia and nitrogen[228]:

$$N_3^- + \tfrac{3}{2}H_2 \rightarrow NH_3 + N_2$$

As the temperature and the duration of the reaction were increased so the decomposition increased. Analysis of the gaseous products did not reveal any hydrazine.

Sodium azide has been found to react with trivalent phosphorus halides to yield phosphinic-nitride polymers[229]:

$$nPBr_3 + nNaN_3 \xrightarrow{165-7^\circ} (Br_2PN)_n + nN_2 + nNaBr$$

$$nC_6H_5PCl_2 + nNaN_3 \xrightarrow{170-5^\circ} (C_6H_5P(Cl)N)_n + nN_2 + nNaCl$$

$$n(C_6H_5)_2PCl + nNaN_3 \xrightarrow{165-7^\circ} ((C_6H_5)_2PN)_n + nN_2 + nNaCl$$

Either the sodium azide is added in small portions to the heated halide or a mixture of azide and halide is slowly heated to the reaction temperature. Nitrogen is evolved in easily controlled reactions.

The reaction between sodium azide and barium carbonate to give cyanide has been used to prepare sodium [^{14}C]cyanide.[231] Thus, sodium azide and barium [^{14}C]carbonate are heated carefully in an atmosphere of nitrogen so as to maintain a steady decomposition of the azide. When the decomposition is complete the residue is heated to dull red heat and cooled; water is then added until all the sodium has reacted, and finally the solution is acidified and the hydrogen [^{14}C]cyanide distilled into an excess of aqueous sodium hydroxide. In this way $78 \pm 2\%$ yields of sodium [^{14}C]cyanide are obtained and the radiochemical yield is about the same as the analytical yield. Since much of the cyanide is formed during the final heating, when no sodium azide is present, it has been suggested that the reaction may involve not the azide but the sodium nitride formed during its decomposition. Modifications to prevent explosions and to increase the yields led to a process in which the reaction was accomplished by fusion at 630° for twenty minutes: yields of 79–85% were obtained.[232] An extension of this principle involves the preparation of [^{14}C]cyanamid (94% yield) from the reaction between sodium azide and barium [^{14}C]carbonate in ammonia.[233]

When equimolecular quantities of iodine monochloride and sodium azide are mixed in carbon tetrachloride at 0° the following reaction takes place[234]:

$$2NaN_3 + 2ICl \rightarrow 2NaCl + I_2 + 3N_2$$

In ether at 0° nitrosyl chloride and sodium azide react thus[234]:

$$NaN_3 + NO{\cdot}Cl \rightarrow NaCl + N_2O + N_2$$

Dry sodium azide reacts explosively with pure chromyl chloride, but with carbon tetrachloride as diluent at 0° a solid, which is probably chromyl azide, $CrO_2(N_3)_2$, is formed.[234, 129]

POTASSIUM AZIDE

The exposure of coarsely crystalline potassium azide to gaseous sulphur trioxide results in the formation of KN_3,xSO_3, where $x \geqslant 4$.[230] This adduct loses sulphur trioxide at room temperature affording potassium azidopolysulphate, $KS_2O_6N_3$, which reacts explosively with water although it does not give rise to a fog in moist air. When kept or carefully heated, potassium azidopolysulphate gives dipotassium trisulphate, $K_2S_3O_{10}$, and pyrosulphuryl azide, $S_2O_5(N_3)_2$. The last is a volatile liquid of freezing point 17°, the boiling point ($>80°$) of which cannot be determined. This is due to explosive decomposition and, moreover, it is advisable that quantities be stored in less than 1 g. samples. Pyrosulphuryl azide in dilute alkali at 0° gives an explosive, milky, crystal-covered layer on the walls of the container. Alkaline hydrolysis gives a mixture containing 15% of sulphate and azide, and 85% of $SO_3N_3^-$; the potassium salt of this ion can be isolated from the solution. Sodium azide behaves analogously to the potassium salt but the reactions are slower.

CÆSIUM AZIDE

The thermal decomposition of cæsium azide has been used to prepare pure cæsium both for calorimetric studies[235] and for reactions with olefines etc.[236]

CALCIUM AZIDE

When calcium azide is crystallized from anhydrous hydrazine the product can be formulated as a dihydrazinate, $Ca(N_3)_2,2N_2H_4$.[237] However, some reaction might have occurred to give the calcium derivatives of 1-pentazene, $HN{=}N{-}NH{-}NH{-}NH_2$, or 2-pentazene, $H_2N{-}NH{-}N{=}N{-}NH_2$, both of which are isomeric with the dihydrazinate.

COMPLEX AZIDES

A considerable amount of work has been done on the use of divers azido-complexes of transition metals in the field of nucleophilic octahedral substitution.[238–248] The azide group has been examined both as a substituting reagent *e.g.*, as in its reaction with *cis*-Co $en_2Cl_2^+$, and also for its labilizing and directing effect in some ions having a co-ordinated azide group, e.g. $[Co\ en_2N_3X]^{n+}$, where X is the group that is replaced by, for example, water (as in octahedral aquation). The azide group is unusual among the ligands studied in that not only does it possess unshared electrons adjacent to the metal, which thereby makes it capable of an electropositive electromeric effect ($+E$) which directly loosens the ligand bond and is *cis*-specific, but it also has a dipolar canonical structure with an electron deficiency adjacent to the metal which allows it to have an electronegative conjugative effect ($-T$), by which it can accept metal electrons. This electron transfer will reduce the density of the unshared metal electrons on the remote side of the complex. In the first case the azide group is similar to the OH, NCS, and Cl ligands, the $+E$ order being: OH > NCS > Cl > N_3. In the second case the azide resembles the nitro group, the well-established $-T$ order being: $NO_2 > N_3$.

In order to avoid complications due to the presence of acidic protons on the non-participating groups and to substitution involving bimolecular solvent intervention, some kinetic studies have been made on *cis*-bis-pyridino-bis-*o*-phenanthroline-ruthenium(II) ions in dry acetone.[248] It was observed that only those anions, such as azide, which have potentially vacant *p*-orbitals for π-bonding engage in bimolecular substitution.

In the absorption spectra of $[Co(NH_3)_5N_3]^{++}$ and $[Cr(NH_3)_5N_3]^{++}$ the higher bands show a greater shift towards the red relative to the hexammine. In the case of the cobalt complex this indicates a stronger metal–nitrogen bond.[249] However, in the reaction of Cr^{++} with $[Co(NH_3)_5N_3]^{++}$ transfer of azide to the chromium occurred.[241]

The equilibrium constants, at 25° and 35°, for the ion-association reactions:

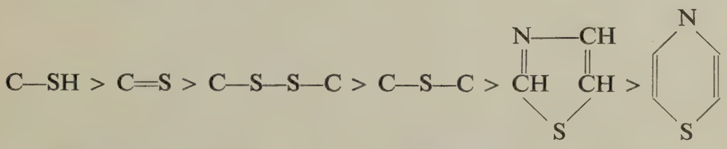
$$[Co(NH_3)_6]^{3+} + N_3^- \rightleftharpoons [Co(NH_3)_6]^{3+}N_3^-$$
$$[Co\ en_3]^{3+} + N_3^- \rightleftharpoons [Co\ en_3]^{3+}N_3^-$$

have been determined and used to derive entropy changes which have been compared with calculated values.[250]

General Reactions of the Azide Ion

THE AZIDE–IODINE REACTION AND RELATED REACTIONS

The oxidation of hydrogen azide by iodine in the presence of sodium thiosulphate was first demonstrated by Raschig (Mellor, VIII, 337). This reaction has since been examined very extensively, both from a mechanistic viewpoint and also to find out which other ions catalyse the reaction. It has been found that the only compounds which act as catalysts are sulphur compounds, and a wide variety of types is known. Since the reaction is characterized by a disappearance of the free iodine it has been made the basis for a variety of qualitative and quantitative estimations. Thus 'spot tests' have been described for the detection of sulphides,[251, 252] thioketones and mercaptans,[252] and several thioethers and heterocyclic sulphur compounds.[253] Convenient methods of detection have also been applied to sulphides, thiocyanates and thiosulphates, and the detection of traces of hydrogen sulphide in water.[254] A useful modification comprises the transformation of inorganic sulphur compounds into the sulphides by melting them with potassium or sodium[255]; and the reaction has been utilized in the micro-determination of sulphide, thiosulphate, and thiocyanate (using a fluorescent indicator)[256] and other sulphur compounds such as cystine.[257–8] The particular advantage of using this method for the determination of cystine lies in the fact that the azide–iodine reaction is not catalysed by any known compound which does not contain a sulphur atom.[258] A very wide range of sulphydryl and other organic sulphur compounds has been studied.[259–263] The following order of decreasing catalytic activity has been published[262]:



The use of cysteine is said to lead to a volume of nitrogen which is given by[263]:

$$V = -33 + 819[SH] + 31{\cdot}5[SH]^2$$

where, V = volume of nitrogen in µl., [SH] = concentration of cysteine in micro-equivalents/ml. If cystine is used then the volume is time-dependent as follows[263]:

$$V = 9 + 1{\cdot}95t[\text{—S—S—}]$$

where, t = time in minutes and [—S—S—] = concentration of cystine in micro-equivalents/ml.

Sodium azide and iodine are decomposed, with the evolution of nitrogen, by 'niello', which is a black metal-like mixture of the sulphides of copper, silver, and lead.[264]

Detailed studies of the catalytic effect of tetrathionate ions,[265] pentathionate ions,[266] and carbon disulphide[267–8] indicate that the following general mechanism applies:

$$\begin{aligned} N_3^- + X^{m-} &\rightarrow N_3X^{(m+1)-} \quad \text{rate-determining step} \\ 2N_3X^{(m+1)-} + I_2 &\rightarrow (N_3X)_2{}^{2m-} + 2I^- \\ (N_3X)_2{}^{2m-} + 2N_3^- &\rightarrow \{2N_3X^{(m+1)-}\} + 3N_2 \\ \{N_3X^{(m+1)-}\} &\rightarrow N_3^- + X^{m-} \end{aligned}$$

where X^{m-} is $S_4O_6^{--}$, $S_5O_6^{--}$, or CS_2.

The rate constants for the hexathionate catalysis of the azide–iodine reaction are almost identical with those for the catalysis by pentathionate, which indicates an almost instantaneous decomposition of the hexathionate, in slightly alkaline solution, to pentathionate and sulphur.[266]

The catalytic effect of trithionate,[269] and monoseleno- and monotelluro-pentathionate ions[270] is ascribed to thiosulphate ions produced by the preliminary decomposition of these ions.

The observation that carbon disulphide is regenerated supports the above mechanism,[267] which is contrary to the earlier observations and mechanism put forward by Browne and Hoel (Mellor, VIII, 338), but agrees with other work.[271]

From the rate-determining reaction given above it can be seen that the reaction rate is proportional to the concentrations of the azide ion and the catalyst. On the other hand it has been stated that the catalytic effect of tetrathionate is affected by the concentration of iodide ion, and that the reaction involving thiosulphate as catalyst has the following mechanism[272]:

$$\begin{aligned} S_2O_3^{--} + I_2 &\rightleftharpoons S_2O_3I^- + I^- \\ S_2O_3I^- + S_2O_3^{--} &\rightleftharpoons S_4O_6^{--} + I^- \end{aligned}$$

This is very similar to the course of the reaction proposed by Raschig (*loc. cit.*). Similarly the reaction between azide, iodine, and thiocyanate is thought to proceed through the formation of an intermediate compound from iodine and thiocyanate.[273]

Other mechanisms proposed for the catalysis of the azide–iodine reaction include a simple electron-transfer process,[274] and also a complex sequence of reactions involving hydrolysis of hydrogen azide to hydrazine and nitrous acid, disproportionation of iodine into I^+ and I^-, etc.[275–6] Thus the following mechanism is proposed to account for the catalytic effect of thiocyanate[276]:

$$\begin{gathered} I_2 \rightarrow I^+ + I^- \\ 2(HN_3 + 2H_2O \rightarrow N_2H_4 + HNO_2) \\ 2(2HNO_2 \rightarrow NO + NO_2 + H_2O) \\ I^+ + SCN^- \rightarrow I + SCN \\ I + SCN^- \rightarrow I^- + SCN \\ 2(SCN + NO \rightarrow SCN^- + NO^+) \\ 2(NO^+ + OH^- \rightarrow HNO_2) \\ 2(NO_2 + N_2H_4 \rightarrow \tfrac{3}{2}N_2 + 2H_2O) \\ 2(H_2O \rightarrow H^+ + OH^-) \\ 2(I^- + H^+ \rightarrow HI) \\ \hline I_2 + 2HN_3 \rightarrow 3N_2 + 2HI \\ \hline \end{gathered}$$

The catalytic effect, on the azide–iodine reaction, of thiosulphate ion adsorbed in precipitated calcium carbonate has also been studied.[277]

In the study of the catalysed azide–iodine reaction it was stated that a mechanism involving the formation of IN_3 was impossible.[267] However, in the thiosulphate- or tetrathionate-catalysed azide–bromine reaction the following mechanism has been proposed[278]

$$N_3^- + Br_2 \rightleftharpoons N_3Br + Br^- \qquad (1)$$

$$N_3^- + N_3Br \rightarrow 3N_2 + Br^- \qquad (2)$$

Equilibrium (1) is said to be attained quickly and equation (2) is held to be the rate-determining step.

From the various rates of reaction the values given in Table III have been calculated for the energy of activation of the catalysed azide–iodine reaction.

Table III.—Activation Energies of Catalysed Azide–Iodine Reactions

Catalyst	Energy of Activation, g.-cal. mole^{-1}	Ref.
Trithionate	19,070	269
Tetrathionate	12,740 (calc., 13,140)	265
Pentathionate	10,970	266
Thiocyanate	20,800	273
Carbon Disulphide	19,950	267

The energy of activation of the spontaneous decomposition of trithionate into sulphate and thiosulphate is 20,650 g.-cal. mole^{-1}, which indicates that the thiosulphate produced is responsible for the catalytic effect of trithionate.[269]

The reactions between azide ions and carbon disulphide, tetrathionate, and thiocyanogen in the absence of iodine have been studied. The reaction of carbon disulphide to form the azidodithiocarbonate ion is second-order with respect to N_3^- and CS_2, and the energy of activation is 21,100 g.-cal. mole^{-1}; this is very similar to the value for the carbon disulphide-catalysed azide–iodine reaction.[279] The difference, i.e. 1150, is said to represent the negative energy of activation of the chain of the catalysed azide–iodine reaction.[268, 279]

In the reaction of tetrathionate ions[280]:

$$S_4O_6^{--} + 2N_3^- \rightarrow 2S_2O_3^{--} + 3N_2$$

only 82–3% of the nitrogen is liberated. This is probably due to the disproportionation of the tetrathionate into the tri- and penta-thionate, which decompose further to sulphur and sulphate. The rate of reaction is decreased by the presence of thiosulphate, which is explained by the assumption that the reaction proceeds in two steps, the first of which involves thiosulphate and is reversible:

$$S_4O_6^{--} + N_3^- \rightleftharpoons S_2O_3N_3^- + S_2O_3^{--}$$

$$S_2O_3N_3^- + N_3^- \rightarrow S_2O_3^{--} + 3N_2$$

The activation energy is calculated to be 23,700 g.-cal. mole^{-1}.

The redox potentials of chloride, bromide, iodide, and thiocyanogen are, respectively, $-1{\cdot}36$, $-1{\cdot}07$, $-0{\cdot}54$, $-0{\cdot}77$; it was therefore predicted that thiocyanogen, which often behaves like a halogen, will oxidize the azide ion to nitrogen.[281] Accordingly a solution of thiocyanogen in carbon tetrachloride was added to aqueous sodium azide, whereupon a brisk evolution of gas, which was shown to be 99·6% nitrogen, occurred. Some spontaneous decomposition of the thiocyanogen took place at the same time and it seems likely that the reaction is catalysed by thiocyanogen as well as by the thiocyanate produced.

THE AZIDE–NITRITE REACTION

The reaction between azide ions and nitrite ions to give nitrogen and nitrous oxide has long been known (Mellor, VIII, 339). It was assumed that nitrosyl azide was formed as an intermediate:

$$HNO_2 + HN_3 \rightarrow NO{\cdot}N_3 + H_2O$$
$$NO{\cdot}N_3 \rightarrow N_2O + N_2$$

This reaction has since been investigated in detail: (*a*) in perchloric acid,[87] (*b*) in a buffer solution,[88] (*c*) with the aid of [^{18}O]water,[89] and (*d*) in an acetate buffer.[90] In each case it was demonstrated that nitrosyl azide was in fact an intermediate and it was shown that it was not hydrolysed but decomposed completely to nitrogen and nitrous oxide:

(*a*) In an excess of aqueous perchloric acid at 0° the reaction is second-order with respect to HNO_2, nearly zero-order with respect to HN_3, and is acid-catalysed. Two main paths are proposed:

$$HN_3 + H_2NO_2^+ \rightarrow NO{\cdot}N_3 + H_3O^+$$
$$N_3^- + N_2O_3 \rightarrow NO{\cdot}N_3 + NO_2^-$$

followed by rapid conversion thus:

$$NO{\cdot}N_3 \rightarrow N_2 + N_2O$$

(*b*) In an excess of sodium azide and hydrogen azide buffer solution the rate-determining step is nucleophilic attack on $H_2NO_2^+$ by azide ion to form nitrosyl azide.

(*c*) The isotopic composition of the nitrous oxide formed by the reaction of nitrous acid and azide in [^{18}O]water was studied at 0° in a solution of pH 5 and in 0·05 M. perchloric acid. The variation of the [^{18}O]oxygen content of the nitrous oxide with the azide concentration and the acidity showed the absence of hydrolysis of the nitrosyl azide but revealed its complete decomposition to nitrogen and nitrous oxide.

(*d*) In acetate buffers at 0° the initial step in the reaction between nitrous acid and azide ion involves the following reaction:

$$AcO^- + H_2NO_2^+ \rightarrow AcO{\cdot}NO + H_2O$$

This is followed by one of two reactions:

$$AcO{\cdot}NO + N_3^- \rightarrow NO{\cdot}N_3 + AcO^-$$
$$AcO{\cdot}NO + NO_2^- \rightarrow N_2O_3 + AcO^-$$

followed by: $N_2O_3 + N_3^- \rightarrow NO{\cdot}N_3 + NO_2^-$

or $N_2O_3 + H_2O \rightarrow 2HNO_2$

The rates of both processes are similar and the nitrosyl azide subsequently decomposes rapidly to nitrogen and nitrous oxide.

The formation of nitrosyl azide and its immediate decomposition into nitrogen and nitrous oxide has also been proposed in order to account for the reaction between nitrosyl compounds and azide ion[86]:

$$NO{\cdot}X + MN_3 \rightarrow N_2 + N_2O + MX$$

where X = BF_4^-, ClO_4^-, HSO_4^-, $\frac{1}{2}S_2O_7^{--}$, $\frac{1}{2}SnCl_6^{--}$, $\frac{1}{2}SbCl_6^{--}$
M = Me_4N, Na

The essential reaction is given simply as:

$$NO^+ + N_3^- \rightarrow NO{\cdot}N_3 \xrightarrow{\text{rapid}} N_2 + N_2O$$

An extension of this is the reaction between ethyl nitrite, sulphur dioxide, and an azide thus:

$$NO{\cdot}OEt + SO_2 + Me_4N{\cdot}N_3 \rightarrow N_2 + N_2O + Me_4N{\cdot}SO_2OEt$$

In an analogous manner the reaction between azide ions and dinitrogen tetroxide to give nitrate, nitrogen, and nitrous oxide was explained on the assumption that the dinitrogen tetroxide is in equilibrium with nitrogen dioxide and with nitrosyl nitrate, $NO{\cdot}NO_3$.

CATALASE, AZIDE AND HYDROGEN PEROXIDE

The inhibition of catalase activity by azide has been studied by many workers.[283–291] The catalase–iron system undergoes an oxidation-reduction cycle accompanied by the oxidation of the azide to nitrous oxide, nitrogen, and water.[288] The azide appears to act as a competitive inhibitor by reversibly forming with catalase a stable complex containing one azide group and at least one hydrogen peroxide molecule.[290] The inhibitory power of the azide ion decreases as the temperature increases.[291] Azide ion and proto- and haemato-haematins form complexes similar to the azide–catalase complex, but with a much reduced affinity.[292]

MISCELLANEOUS

The reduction of hydrogen azide by an acidic solution of chromium(II) chloride to ammonia and nitrogen (Mellor, VIII, 340) has been examined further. It was found that two chromium(II) ions were consumed by each azide ion or hydrogen azide molecule[293]:

$$2Cr^{2+} + 2H^+ + HN_3 \rightarrow 2Cr^{3+} + NH_3 + N_2$$

In the presence of aqueous perchloric acid this reaction was confirmed but it was observed that the ammonia is co-ordinated with the chromium(III) ion.[294] It was further shown that three complex ions were produced, namely: hexa-aquochromium(III), penta-aquomonoamminechromium(III), and a binuclear chromium(III) ammine thought to be $[(H_2O)_5Cr{-}NH{-}Cr(H_2O)_5]^{4+}$.

The addition of 0·0882 g. of azide ion in the form of sodium or potassium azide to 10 ml. of 1% quinine sulphate suppresses the fluorescence completely and this amount is almost exactly the same as that of chloride, bromide and iodide, whereas 1·52 g. of fluoride ion is required.[295]

Azide ions are said to reduce polyacrylonitrile radicals in aqueous solutions,[296] and studies have also been made of the photochemical reduction of water by azides, etc., in the presence of acrylonitrile or methyl methacrylate.[297] Ultra-violet irradiation (300–400 mμ) of the system Fe^{3+}–azide–monomer has been studied and the quantum yield of ferrous ions was found to vary linearly with the concentration of monomer, unlike the systems involving chloride or hydroxide where the yield was independent of the monomer concentration.[298] The results were explained in terms of the presence of organic radical fragments originating from impurities.

The electrolytic discharge of azide and hydroxide ions has been viewed in the light of a general equation for anodic overvoltage.[299–300] It has been shown that below 12° hydroxide ions are discharged, and above 18° only azide ions are discharged from an aqueous solution of azide.[301] The anodic deposition of azide from aqueous solution at platinum,[302–3] palladium,[303] and iridium[303] electrodes shows the characteristics of activation overpotential and the potential, π, varies linearly with the logarithm of the current density, i, in the Tafel relationship for substantially irreversible processes:

$$\pi = a + b \log i$$

where $a = 1{\cdot}1$, $b = 0{\cdot}59$.[302]

The process:

$$N_3^- \rightarrow \tfrac{3}{2}N_2 + e$$

is irreversible but it is estimated that the reversible potential for unit activity of N_3^- is $-3{\cdot}3$ v. with respect to a normal hydrogen electrode.[303]

The pyrolysis of azides at 265–275° affords activated nitrogen, the half-life of which has been found to be *ca.* 16–40 sec./10^{-4} mm.[304] The activation energies, 23–45 kcal., were found to be independent of the cation of the azide and the emission spectra for all the azide pyrolyses studied each had the same characteristic five bands: 1975 ± 25, 2150 ± 25, 2300 ± 35, 2400 ± 40, and 2550 ± 50 A.

Glow-discharge electrolysis of aqueous azide solutions has been examined: the electrolysis is accompanied by oxidation arising from the decomposition of water molecules caused by the bombardment of the solution by gaseous ions, and the chemical phenomena are analogous to the effects produced by ionizing radiations.[305]

The photochemical, thermal, and electrolytic decomposition of azides has been reviewed and a general mechanism adduced, which depends on a chain reaction propagated by an electronically activated nitrogen species[306]:

$$\begin{gathered}
MN_3 \rightarrow N_2^* + MN\langle \\
N_2^* + MN_3 \rightarrow N_2 + N_2^* + MN\langle \\
N_2^* \rightarrow N_2 + h\nu \\
MN\langle + MN\langle \rightarrow N_2 + 2M \\
\hline
MN_3 \rightarrow \tfrac{3}{2}N_2 + 2M + h\nu
\end{gathered}$$

In a study of the group-electronegativity of inorganic groups the azide group was found to have the value 2·95, which is in accord with the average of 3·0 derived from the value for nitrogen.[307]

Thermochemistry, Photochemistry and Explosive Decomposition

STRUCTURE AND STABILITY

The relationships which exist between the structure, stability, and thermal, photochemical, and explosive decompositions of the metal azides have been extensively investigated and reviewed.[2, 308–10]

One of the earliest studies in this field involved the construction of Morse curves for the formation of molecules from ions, neutral atoms, and radicals.[311] The results qualitatively indicated that the stability of metal azides decreases with an increase in the ionization potential of the cation. Although this treatment did not consider the solid lattice, more precise calculations have substantiated and extended the theory.[49, 114, 312] The thermal decomposition of metallic azides proceeds initially from the transfer of an electron from the valence band into the conduction band, which in so doing results in the formation of a neutral azide radical. The azide ions will be converted into radicals more easily as the influence exercised on the valence electrons by the metal increases; that is to say the higher is the ionization potential of the metal the greater is the effect. The series most commonly considered is: KN_3, TlN_3, AgN_3, CuN_3; the ionization potential of the metal increases along this series as also does the deviation from an ionic structure, and the increased tendency toward neutrality of the azide entity results in the observed increase in explosive properties. Associated with these trends are a decrease in the decomposition temperature, and increases in the refractive index, lattice energy, and enthalpy of formation (see Table IV).

The correlation of refractive index with azide structure has been explained in the following terms[308]:

(*a*) ~1·5, no variation with inclination of the electric vector: Typical ionic structure.

(*b*) ~1·8, close packing of spherical ions.

(*c*) >1·8, with variation with inclination of the electric vector: Directed bonding structure.

Table IV.—Comparative Properties of Azides

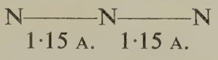
	Ionic Radius (A)	Ionization Potential (eV)	Lattice Energy (kcal. mole^{-1})	Refractive Index	Enthalpy of Formation (kcal. mole^{-1})	Decomp. Temp. (°C.)
KN_3	1·33	4·34	157	1·45, 1·66	−0·33	350
TlN_3	1·51	6·11	163·5	>1·99	55·7	334
AgN_3	1·26	7·54	205	>2, 1·8	74·2	250
CuN_3	0·96	7·73	227	>1·8	67·2	205

THERMODYNAMIC PROPERTIES AND STABILITY

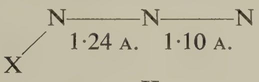
It has been emphasized that an overriding criterion for an azide to be explosive is that the enthalpy of formation, ΔH°_f, must be positive,[313] and it is in fact found that the most endothermic azides have the highest explosive sensitivity. Now the enthalpy of formation of the crystalline azide and the ionization potential of the metal, I(M), are related in the Born–Haber cycle by the equation:

$$\Delta H^\circ_f(\mathrm{MN_3})_s = I(\mathrm{M}) + L(\mathrm{M}) - U(\mathrm{MN_3}) - 2RT + \Delta H^\circ_f(\mathrm{N_3})_g - E(\mathrm{N_3^-})$$

where $U(\mathrm{MN_3})$ is the lattice (internal) energy of the azide. It can be seen that the first three quantities on the right-hand side of the equation are dependent on the metal, whereas the remaining three are independent of the cation. Of the three dependent quantities the largest numerical variation is found in I(M) and because of this correlation between I(M) and $\Delta H^\circ_f(\mathrm{MN_3})_s$ it is to be expected that there should be a close relationship between the ionization potential and the explosive nature of the azide. It was also emphasized that the deviations from ionic binding do not produce bonds which are covalent in the same way that hydrogen azide and the organic azides are covalent. In the latter compounds the symmetrical nature, I, of the azide ion is lost and is replaced by the asymmetric form, II:



I



II

(For a discussion on the structure of these compounds in the light of Pauling's 'Adjacent Charge Rule' see ref. 314). The difference between the structures of the

Table V.—Physical Properties associated with Explosive Decomposition of Azides

	Cation		Lattice Energy (kcal. mole^{-1})	Enthalpy of Formation (kcal. mole^{-1})	Decomposition Temperature (°C.)
	Ionic Radius (A.)	Ionization Potential (ev.)			
Li	0·60	5·39	194	2·58	
Na	0·95	5·14	175	5·08	275
Rb	1·48	4·18	151·5	−0·07	321
Cs	1·69	3·89	145·5	−2·37	326
NH_4	1·48		175	26·79	160 (subl.)
Cu(II)		7·73		140·4	
Hg(II)	1·10	10·41			190
Hg(I)	1·25	10·41		141·5	210 (230)
Ca	0·99	6·11	517	11·03	
Sr	1·13	5·69	494	1·72	
Ba	1·35	5·21	469	−5·32	275
Pb	1·20	7·41	516	115·5	250

two types of azide has a profound effect on their modes of decomposition. Thus the decomposition of the metal azides is interpreted in terms of azide radical formation whereas the first step in the decomposition of covalent azides is always fission of the longest N—N bond with the formation of a diradical and a molecule of nitrogen.

The information given in Table V supplements that in Table I[7, 49, 126, 188, 315–8]

The standard enthalpy of formation of the azide is estimated to be 115 kcal. mole^{-1}[188]; the excellent agreement of this figure with the earlier[319] calculated figure of 133 kcal. mole^{-1} was said to be partly fortuitous since the numerical results used in the earlier calculation were not derived from first principles. Included in Table VI are enthalpy data for hydrogen azide, gas and liquid, and the aqueous azide ion:

Table VI.—Enthalpies of Formation of Azide Species

Enthalpy of Formation (kcal. mole^{-1})			
HN_3 (g)	71·66	N_3 (radical)	115
HN_3 (l)	64·37	N_3^- (aq.)	65·53

From the values given in Tables V and VI the corresponding free energy and entropy values have been derived.[7, 320]

From the enthalpy of formation of the azide radical the bond dissociation energies of some covalent azides were derived for a series of aliphatic azides. The mean value was 83 kcal. mole^{-1}, which is very similar to those obtained for methylamine (80), ethylamine (78), and aniline (91) and it seems likely that the C—N bond dissociation energies in azides do not differ significantly from those in the corresponding amines.

The electron affinities and ionization potentials (I) of some atoms, ions and radicals which form azides are listed in Table VII.[7, 49, 114, 188, 308–315]

Table VII.—Electron Affinities and Ionization Potentials of Azide-forming Ions and Groups

	Electron Affinity (ev.)	1st Ionization Potential (ev.)
K	0·70	4·34
H	0·75	13·52
$(C_6H_5)_3C$	2·1 ± 0·2	—
Me	~1·1	~10·0
NO	>0	9·5
I	3·24	10·6
Br	3·55	11·8
CN	3·61 ± 0·39	14·0
Cl	3·84	12·95
F	3·63	17·34
SO_2	2·81	13·1
CO	—	14·1
N_3	3·52	11·6
CNS	3·49	—
1 ev. ≡ 23·05 kcal. mole^{-1}		

In connection with the effect of increasing ionization potential on the explosive sensitivity of the 'ionic' azides it can be seen that hydrogen, $I = 13{\cdot}52$ ev., represents an extreme case. While the structure of solid hydrogen azide is unknown, the iso-electronic cyanic acid, HCNO, shows a large deviation from an ionic structure and has considerable molecular bonding.[114] As the ionization potential and electron affinity of a group increase, structure and electron distribution change from ionic compounds like potassium azide through covalent compounds such as methyl azide, at about $I = 9$ ev., and finally to the halogen azides which are probably polarized thus $Cl^{\delta-}N_3^{\delta+}$.[308, 312]

The specific heats of silver and lead azide are quoted in Table VIII[321]:

Table VIII.—Specific Heats of Silver and Lead Azide

Initial Temperature	100	200	250°C.
PbN_6	0·100	0·117	0·116 cal. g.$^{-1}$ °C.
AgN_3	—	—	0·117

Lead azide pressed into a pellet with the aid of a little paraffin has a coefficient of thermal conductivity of $4{\cdot}2 \times 10^{-4}$ g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$; if the paraffin is not used the value is $1{\cdot}55 \times 10^{-4}$.[322] More accurate measurements have been made on the azides of sodium, thallium(I), barium and lead.[323] The values obtained are 25×10^{-4} (68°C.), 8×10^{-4} (65°), 11×10^{-4} (80°), and 4×10^{-4} (45°) g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ respectively.

Some precise work using metal–metal azide electrodes has been accomplished which has enabled accurate calculations to be made for the standard free energies of formation, ΔG°_{298}, recorded in Table IX[214, 215]:

Table IX.—Free Energies of Formation of Azides

	AgN_3	TlN_3	HgN_3	PbN_6
ΔG°_{298}	78·69	59·17	77·3	126·3 kcal.

The same work gave the corresponding entropies and enthalpies to a high degree of reliability and accuracy. Similar electrodes have been used in the determination of the standard electrode potentials of thallium(I) and azide ions, their individual ion activities and the mean activity of thallium(I) azide solutions. Reported values of E_o are: E_{Tl^+}, $-0{\cdot}3339$; $E^c_{N_3^-}$, $+0{\cdot}2948$; and E^0, $-0{\cdot}6298$ v. respectively.[324–7] Various thermodynamic quantities for the ion pair TlN_3 have been measured by means of solubilities of thallium(I) iodate in sodium azide at 10, 25, and 40° (see Table X)[328]:

Table X.—Thermodynamic Quantities for the Thallium Azide Ion Pair

	ΔG_{25}	ΔH	ΔS	$S_g(TlN_3)$	$\Delta S(g)$	ΔS(hyd.)	$r_c + r_a$
	kcal. mole^{-1}		g.-cal. deg.$^{-1}$ mole^{-1}				A.
$Tl^+N_3^-$	$-0{\cdot}53$	$-1{\cdot}33$	$-2{\cdot}7$	66·7	$-25{\cdot}2$	$-7{\cdot}0$	$\sim 3{\cdot}1$

THERMAL DECOMPOSITION

The thermal and photochemical decomposition have been the subject of much study, both from the particular behaviour of individual compounds and also as part of wider studies embracing the general theory of explosions and of detonation.[2, 308–10, 329–30]

The simplest result of the decomposition of the metallic azides is the evolution of nitrogen and the formation of the free metal:

$$2MN_3 \rightarrow 2M + 3N_2$$

Sometimes, however, the metal nitride is formed at the expense of the metal.

The thermal decomposition of sodium and potassium azides, the rate of which is directly proportional to the time, is catalysed by the vapour of the metal and if this vapour is continuously removed then the rate of reaction is much slower.[331–2] The activation energies for the decompositions are: for sodium azide, 33·4 (at 240–275°), and 36·1 (24·8 mm. potassium vapour, 220°); for potassium azide, 41·5 (16·4 mm. potassium vapour) kcal. mole^{-1}. The reduction in this activation energy as the pressure of metal vapour increases is said to be the reason for the catalytic effect.[332] The decomposition of potassium azide has been interpreted in terms of *F*-centre formation and decay.[332] The decomposition of sodium azide is said to proceed in two stages each with distinct energies of activation, and there is evidence for two forms of sodium azide with a transition temperature ~365°.[333–5] The energies of activation for the decomposition of these two forms are given as 46[333] and $50 \pm 1{\cdot}3$[335] kcal. mole^{-1} above the transition temperature, and 23[333] and $27{\cdot}6 \pm 1{\cdot}6$[335] kcal. mole^{-1} below this temperature.

The alkaline-earth metal azides decompose by a mechanism different from that of the alkali-metal azides but there is disagreement over the pressure–time relation. When the pressure of nitrogen, p, evolved is measured against time, t, it was found that the equation:

$$\log p = kt + \text{constant}$$

held for calcium,[336] strontium,[337] and barium[338] azides, the respective activation energies being 18–19, 20, and 21–27 kcal. mole^{-1}. However, later workers have demonstrated that the pressure is proportional to t^3 in the case of calcium[339] and strontium[339] and to t^6 for barium azide.[339–341] Other investigations have been made into the decomposition of calcium,[343–3] strontium[343] (irradiated and non-irradiated), and barium[345–9] azides and the alternative mechanisms discussed.[2, 350] A comparison has been made between the explosive characteristics of the alkaline-earth metal azides under various conditions.[351] The formation of nitrides during the decomposition of calcium[342] and barium[345–6] azides is well known, and the explosive nature of these azides has been discussed in relation to the heat of formation of the nitrides.[2, 308] The heats of decomposition to the metal and to the nitride of some azides are listed in Table XI:

Table XI.—Heats of Decomposition of Azides

	$-\Delta H$ of decomposition kcal. mole^{-1}	
	to metal	to nitride
LiN_3	2·6	18·8
$Ca(N_3)_2$	11·0	45·4
$Sr(N_3)_2$	1·7	32·8
$Ba(N_3)_2$	−5·3	23·6
$Pb(N_3)_2$	115	
TlN_3	56	
AgN_3	74	
CuN_3	67	
$Cu(N_3)_2$	140	
Hg_2N_6	141	

DECOMPOSITION IN THE PRESENCE OF OXYGEN

In air or oxygen the decomposition is even more rapid since the decomposition to the oxide is considerably more exothermic.[352] It has been suggested that the formation of the nitride from the alkaline-earth metal azides results from the reaction between the metal first formed and unchanged azide.[342, 345–6] A later view is that formation takes place by reaction of the metal with gaseous nitrogen.[353] The thermal decomposition of barium azide under decalin has been studied and the following reaction proposed[354]:

$$3Ba(N_3)_2 \rightarrow Ba_3N_4 + 7N_2$$

Time–pressure studies on the thermal decomposition of silver azide indicate several alternative kinetic equations.[115, 355–8] The activation energy is 35–40 kcal. mole^{-1}.[355–6, 359] and it was found to be unaffected by the incorporation of foreign ions into the silver azide lattice.[115, 356] Such a sensitized azide does however decompose at a lower temperature and a much greater rate (see Table XII)[115]:

Table XII.—Decomposition of Silver Azide

Temperature of Decomposition	260°	270°	280°
pure AgN_3	280 sec.	140 sec.	70 sec (explodes at 340°)
$CN_2^{--}:N_3^-:Ag^+ = 1:10:20$	10	5	
$CN_2^{--}:N_3^-:Ag^+ = 1:5:5$	1	explodes	

The proposed mechanism of the decomposition involves the production of free electrons,[360] and the promotion of an electron into the conduction band[357] with subsequent combination of two azide radicals thus:

$$N_3^- \rightleftharpoons N_3 + e$$

$$2N_3 \rightarrow 3N_2 + 210 \text{ kcal.}$$

The decomposition of silver azide has been studied with an electron microscope; although the electron beam caused some decomposition it was found possible to follow nucleation.[361] The effect of a small amount of cadmium ($6 \times 10^{-5}\%$) in a silver azide lattice has been studied: in spite of a large increase in detonation velocity no detectable change in the *X*-ray pattern could be seen.[362] During the measurement of the electrical conductivity of single crystals of silver azide it was found that when there was a potential of 45 v. placed across the crystal, a current of 180 μA. produced an explosion after several minutes.[363]

The decomposition curves, *in vacuo*, of α-lead azide are sigmoid in character, indicating an autocatalytic reaction, and the final product is metallic lead.[364] In air at 240° α-lead azide is said to give tetragonal lead oxide as the final product, and two intermediate basic lead azides have been observed.[365] The extension of the thermal decomposition in air to studies at 150, 175, and 200° enabled characteristic decomposition curves to be drawn.[366] These curves were notable for being 'stepped' and not smooth and the various steps were considered to be associated with definite crystal phases. The effect of the presence of dry oxygen was investigated: whereas in air the first step corresponded to a 12% loss in weight and further losses followed, it was found that in dry oxygen or argon a smooth curve was obtained up to the 12% loss after which the weight remained constant.[367] It was concluded that further decomposition can take place only in the presence of moisture. If layers of lead were formed, as had been proposed,[368] it was thought that these would react immediately with the oxygen and result in entirely different decomposition characteristics. It was also suggested that the mechanism for the decomposition is dependent on the temperature and therefore the time-to-ignition. If the temperature is too low for sufficient activated centres to be formed then a chain reaction will not be set in operation and a slow stepwise decomposition will result. The influence of definite concentrations of moisture on the thermal decomposition of α-lead azide has been studied.[369] The water vapour was held responsible for the 'poisoning' of the autocatalytic nuclei and a general theory was developed to account for the observed differences in the induction periods for different azides. Thus, it was said that in a vacuum system the water-vapour pressure of $\sim 10^{-4}$ mm. was too low to prevent the 'germ-nuclei' from growing. However, in the case of the alkali and alkaline-earth metal azides the long induction periods could be attributed to the fact that the high reactivity of these metals results in the very small amount of moisture, present even in vacuum systems, sufficing to react with all the nuclei. Conversely, the absence of an induction period in silver azide can be attributed to the lack of reactivity of the metal. The induction period of the decomposition of lead azide can be reduced by coating the azide with metallic silver which probably acts catalytically *via* formation of some silver azide.[370] In a similar way the enhanced sensitivity of lead azide detonators with brass containers may be explained by the formation of copper(I) azide.[105] The decomposition of α-lead azide has also been investigated by other workers,[371–3] and the minimum explosion temperatures for the pure and dextrinated forms are 315° and 275° respectively.[372–3] The activation energy for the decomposition of lead azide in impact tests is 55 kcal. mole^{-1}.[359]

EXPLOSIVE DECOMPOSITION

As an extension of the remarks made earlier on nitride formation from the alkaline-earth metal azides, it has been found that the heat of explosion of lead azide admixed with powdered boron, beryllium, aluminium, magnesium, and zirconium is higher than for the pure azide.[374] The heats of formation of the nitrides of these compounds, which are responsible for this observation, are $-26{\cdot}7$, -135, $-57{\cdot}6$, $-110{\cdot}7$, and 72 kcal. mole^{-1} respectively.

The correlation of explosive sensitivity with ionization potential[49, 114, 312] has been examined in a series of cobalt ammine azides.[141, 375] The compounds tested ranged from the 'purely' ionic hexamminecobalt(III) azide, $[Co(NH_3)_6](N_3)_3$, to the completely co-ordinated triamminetriazidocobalt $[Co(NH_3)_3(N_3)_3]$. The results given in Table XIII were obtained in a falling-hammer test.

Table XIII.—Explosive Sensitivity of Cobaltammine Azides

Compound	Observation
$[Co(NH_3)_6](N_3)_3$	Weak→moderate; 5–75% of sample consumed
$[Co(NH_3)_5N_3](N_3)_2$	Violent, 90–100% consumption
cis-$[Co(NH_3)_4(N_3)_2]N_3$	Violent, complete consumption
trans-$[Co(NH_3)_4(N_3)_2]N_3$	
$[Co(NH_3)_3(N_3)]$	

It is of interest to note that the completely shielded ionic azide ignites at quite low heights, which probably indicates a high heat of reaction following on from impact generated hotspots.

The effect of pressure on the thermal decomposition of the azides has been studied with the general result that as the pressure increases so the ability to explode decreases and at pressures of several thousand kg. cm.$^{-2}$ practically all the mechanical effects of explosion vanish. Also, at the other end of the pressure scale, at pressures below 0·02 mm. the complete decomposition of lead azide could not be initiated.[376–383] Further, as the pressure increases so the temperature necessary to effect decomposition increases,[381–3] *e.g.*, the decomposition of barium azide is effected within three minutes at the following temperatures and pressures[381]:

Pressure	Atmospheric	2,000	10,000	45,000 kg.cm.$^{-2}$
Temperature	170°	210°	225°	235°

The mechanism of the explosive decomposition of azides has been discussed at length.[113, 117, 308–10, 384–99]. The mechanism, both for thermal and for shock initiated explosions, involves the generation of a hot-spot which must be above a critical size, be at about 500°, have a lifetime of ~10–100 μsec., and sometimes be molten. The thermal constants of the material define the life cycle of the hot-spot, from which heat must be lost at a lower rate than it is generated if growth is to occur. The theory of detonation of azides has also been widely studied.[400–13] Various experimental techniques have been described for the measurement of velocities of detonation, the sensitivity of azides to impact, and explosion pressures,[414–9]. The detonation of lead azide, as befits its commercial importance, has been widely studied.[420–31]. The luminous phenomena produced when granules of lead azide are arranged in a ring and detonated from one point have been studied in the presence of various gases with the aid of a microscope.[421–2]

PHOTODECOMPOSITION

The effects of neutron and *X*-ray irradiation on azides have been observed in the solid state,[392, 432–5] in solution,[436] and in gelatin suspensions (of silver azide).[437–8]

The photochemical decomposition of alkali and alkaline-earth metal azides has been the subject of a kinetic study based on[439]:

(i) the rate of evolution of nitrogen;
(ii) the intensity of the radiation;
(iii) the extent of decomposition;
(iv) the nature of the light source (mostly 2537 A.).

This work has shown that the earlier mechanism[440–3] involving exciton formation and subsequent (bimolecular) reaction at imperfections to give nitrogen is inadequate. The results were interpreted as indicating the formation and reaction of both excitons and positive holes. A suggested mechanism is based on the entry of a photon into the crystal lattice and initiation of energy transfers, the net result being the release of nitrogen from the crystal surface.[444]

The photolysis of silver azide reveals that a critical amount of light exists, below which explosion does not occur.[445] The photoconductivity of silver azide and its optical properties have been studied.[446–8] The use of the photochemical properties of silver azide in sensitive emulsions, etc., has been discussed.[449–51]

The decomposition of thallium(I) azide to metallic thallium and nitrogen has been investigated as a function of the wave-length, the light intensity, and the temperature.[448] The refractive index is 2·14 ± 0·05 (sodium light, 5890 A.) and the high- and low-frequency dielectric constants are 4·58 and 11·5 (at 1·35 mc/s.), respectively.[448]

Mercury(I) azide is much more sensitive to light than silver azide and rapidly turns orange-yellow when exposed. The bonds in this compound are predominantly covalent and the photochemical decomposition characteristics are very similar to those of triphenylmethyl azide, the first step probably involving fission of the longest N—N bond.[126]

The photochemical decomposition of lead azide has been examined in the light of photo-induced disproportionation to PbN_{12} and its subsequent breakdown to PbN_6.[444] The behaviour of lead azide–gelatin emulsions has been examined and a strong tendency towards layer separation observed. The sensitivity towards *X*-rays was found to be less than that of silver azide.[452–4]

The photolysis of hydrogen azide at liquid nitrogen temperatures produced imine radicals.[455–6] Further reactions of this radical involve the production of the radical, HN_2, which is responsible for the colour and the paramagnetism of a blue solid observed in the mixture; this solid, suggested as $NH{:}\overset{+}{N}H.\overset{-}{N}H$, reacts with the imine to form ammonium azide. This reaction was said to be the main contributor to the production of ammonium azide under the above conditions.

The photolysis of solutions of hydrogen azide and its salts has been interpreted in terms of a chain reaction, with activated nitrogen (half-life ~5 min.) as the chain carrier.[457] The reaction has been investigated by following the alteration in the pH of the solution and by colorimetry using the ferric–azide complex.[458–61]

ELECTROLYSIS

When the metallic azides undergo *slow* thermal decomposition,[462–74] or when their aqueous solutions are electrolysed[471, 473–81] an emission of ultra-violet radiation is observed. It was found that this radiation was limited to broad bands at about

2000, 2150, 2300, 2400, and 2550 A., and it was suggested that these could be interpreted in terms of the known energy levels of nitrogen. It has since been suggested that these broad features arise from the groups of bands of the nitrogen Vegard–Kaplan system ($A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$), which originate from the $v'=0$, 1, 2, 3 levels of the $A^3\Sigma_u^+$ state.[474] It was also suggested at the same time that the bands produced during the electrolytic experiments are excited in electrical discharges in the small bubbles of nitrogen liberated at the anode. It was pointed out that electrical discharges similar to those in an ozonizer caused by surface changes in such bubbles are known to give rise to the emission of light, and that such discharges are favourable for the excitation of the Vegard–Kaplan system.

SPONTANEOUS EXPLOSIONS

The phenomenon of spontaneous explosions is well known in the field of azide chemistry.[482] It has been widely assumed that α-lead azide is not prone to this phenomenon, in spite of the fact that the heat liberated ($-\Delta H_p$) when one mole of α-lead azide is formed by crystallization is 15·94 ± 0·10 kcal. mole^{-1}, while for the β-form the value is only 0·3 higher. These figures are not abnormally large (*cf.* AgN_3, 16·67; and Hg_2N_6, 29·87), and it has been reported that spontaneous explosions have in fact been observed with α-lead azide growing in an azide–acetate solution, and that the sensitivity of the two forms is approximately the same.[396] A violent explosion was noted when a cadmium rod was immersed in 4% aqueous hydrogen azide for ~30 min.[483] When β-mercury(II) azide is prepared in a diffusion apparatus such as is used for β-lead azide, spontaneous explosions occur which are more violent than those of the latter compound.[483] Spontaneous explosions have also been observed with: ClN_3, BrN_3, IN_3, CuN_6, SiN_{12}.[482]

APPLICATIONS

By far the major use of the inorganic azides depends on their explosive nature. Even as long ago as 1926 it was stated that lead azide was becoming a serious competitor to mercury fulminate for detonators.[484] Although the detonation characteristics such as heat of explosion, temperature of explosion, impact sensitivity, etc., are poorer for lead azide than mercury fulminate[485–6] (see Table XIV) tests in actual use always reveal the superiority of lead azide.[487–9] Moreover, detonators based on lead azide were still functional after fifty-eight days' exposure to a moist atmosphere whereas mercury fulminate based detonators completely failed after seven to twenty-one days of such exposure.[490]

Table XIV.—Comparison of Lead Azide and Mercury Fulminate

	Lead Azide	Mercury Fulminate
Maximum density	4·71	4·42
Gas volume, *l*	308	315
Heat of explosion, kcal.	367	429
Velocity of detonation, m./sec.	5400	5400
Temperature of explosion, °C.	345	445
Sensitivity (2 kg. wt.) cm.	5	3 (calc.)

As may be expected the patent literature abounds with improvements and modifications to detonating compositions containing lead azide.[491–501] These are mainly concerned with reducing the flash point (330°) and with the formulation of the lead azide in a more easily handled form. The effects of compositing pressures on lead azide and mixed charges has been discussed.[502] The use of silver azide as a detonator has also been recommended.[503]

An extension of the gaseous decomposition of azides is the use of calcium, barium, or sodium azides for the production of cellular rubber.[504] Thus, calcium azide (3 parts), crude rubber (100 parts), and various additives when vulcanized at 100° for *ca.* twenty minutes gave a stain-free cellular rubber having a density of 0·27 and a tensile strength of 21 kg. cm^{-2}.

Barium and strontium azides are used as 'getters' in the preparation of electric discharge tubes, and also in improving the performance of the electrodes used in such tubes.[505–508]

Salt mixtures containing sodium azide are used for the purification of molten aluminium and silicon-containing aluminium alloys.[509–10]

Several azides, such as sodium, potassium, barium, and tetramethylammonium azide, are effective in preventing the rusting of iron.[511–3] The effectiveness is enhanced if the solution is made slightly alkaline by, for example, phosphate ions.

Azide ions readily form one half of a redox system for the initiation of polymerization; other suitable components are *p*-toluenesulphinic acid,[514] and oxidants such as MnO_4^-, ClO^-, IO_3^-, BrO_3^-, Ce^{4+}.[515]

A mixture of sodium azide and an alkali metal bicarbonate and hydroxide, when formulated to have pH 9–12, satisfactorily prevents or reduces coagulation of styrene–butadiene latex during storage in contact with metals.[516]

The sensitivity of silver bromide emulsions is enhanced by the addition of silver azide; the addition of oxalic acid increased the azide–bromide emulsion sensitivity even further.[517] Emulsions of this type are sensitive to γ-rays from ^{60}Co for doses over 10^4 r., and are useful for the dosimetry of high-energy radiation.

The effect of sodium azide as a fungicide in wine preservation is said to be highly specific.[518–9]

ANALYTICAL ASPECTS

A number of reactions of the azide ion which may have analytical application are considered under 'Chemical Properties, General Reactions', p. 37. Analytical chemistry of a more specific nature is discussed below.

Acidification of an azide solution and distillation of the resulting hydrogen azide into a known volume of standard sodium hydroxide, followed by back-titration using phenolphthalein as indicator, is said to be a satisfactory analytical method.[520] Sommer and Pincas (Mellor, VIII, 340) found that cerium(IV) salts, in neutral or acidic solution, completely oxidize hydrogen azide to nitrogen, and it was suggested that this could form the basis of an analytical method which involved the measurement of the volume of nitrogen liberated. Convenient procedures have since been devised to enable this to be accomplished to a high degree of accuracy.[520–3] For example, 15 mg. of lead azide completely reacts with 3 ml. of 15–30% cerium(IV) ammonium nitrate within two minutes[523]:

$$2Ce(NH_4)(NO_3)_5 + Pb(N_3)_2 \rightarrow 2Ce(NO_3)_3 + Pb(NO_3)_2 + 2NH_4NO_3 + 3N_2$$

Use of a modified Carson's gas analyser enables the determination to be accomplished simply and rapidly with an accuracy of $\pm 0{\cdot}1\%$; copper(II) and sodium azides can be determined by the same method. A modification involves the use of an excess of the cerium(IV) solution and determination of the excess by titration with ferrous sulphate.[524] This method is said to be more convenient than refined gasometric procedures but the results are not as precise. A method has been developed in which azides in organic solvents can be determined.[525] Thus, the azide (1–20 mg.) is isolated as silver azide from a single-phase solution of the solvent, ethanol, and water. The precipitate is washed free from solvent and oxidized with 0·01 N. cerium(IV) in sulphuric acid; the excess of the oxidizing agent is determined by titration with ferrous ammonium sulphate. The accuracy of the method is said to be better than 1% for 5–20 mg. of N_3^-, and to improve as the concentration increases; the effects of different solvents and foreign ions have been studied.

The oxidation of azides by nitrous acid (Mellor, VIII, 339) has been developed as an analytical method for the determination of milligram amounts of azide.[526] Potassium permanganate also oxidizes azides (Mellor, VIII, 340) and by using it a suitable analytical method has been devised.[527]

Azides have been analysed by titration with silver nitrate in the presence of an adsorption indicator. It was found to be an improvement if the azide solution was added to a solution of a known amount of silver nitrate.[528] An alternative method employs the reaction of the azide with an excess of silver chromate, when the liberated chromate can be determined by titration with quinone, either potentiometrically or by means of diphenylamine.[529] Lead azide, dissolved in barium nitrate containing a little nitric acid and sodium acetate, has been potentiometrically titrated with silver nitrate with an accuracy stated to be 0·5% assuming that the volume reading is accurate to 0·01 ml.[530] Further work has shown that provided the solution is at least 10^{-2} M. in azide then the concentration can be determined by potentiometric titration with silver nitrate.[531] Furthermore, it is advisable to use acetic acid as a medium for quantitative precipitation of the silver azide since nitric acid, even when very dilute, results in dissolution of some of the precipitate.[531] 0·1 M. Sodium azide has been successfully titrated with 0·1 N. silver nitrate by the technique of polarization titration using a silver electrode.[532]

The catalysis of the azide–iodine reaction (*cf.* page 37) has been extensively used for the determination of both azides and the various catalysts. Thus, if a solution containing sodium azide is added to a mixture of carbon disulphide, acetone, and an excess of standard iodine solution then the azide can be determined by the titration of the excess of iodine with arsenite solution.[271] Methods have also been developed which depend on the measurement of the volume of the nitrogen liberated in this reaction. In this way thiocyanate,[533–5] sulphide,[535–6] thiosulphate,[535] thiourea,[537] and glutathione[538] have been accurately determined. The lower limit for the detection of thiocyanate at pH 5·8 by this reaction[539] is 0·035 μg. (as KCNS), at a concentration limit of $1:10^6$. It was shown that at this pH the inhibitory effect of phosphate and ferrocyanide disappears.

A Kjeldahl digestion procedure has been developed which enables the determination of azides, in 10–15 mg. samples, to be satisfactorily accomplished.[540]

Three methods were examined for their suitability for the analysis of technical sodium azide[541]:

(1) Addition of excess of silver nitrate, filtration, and titration of the remaining silver nitrate with potassium thiocyanate.
(2) Decomposition of the sodium azide with an excess of sodium nitrite and sulphuric or hydrochloric acid and titration of the unconsumed acid:

$$NaN_3 + NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + N_2 + N_2O$$

(3) Use of the catalysed azide–iodine reaction.

For the above purpose method (2) was found to be the most satisfactory.

The analysis of technical lead azide is carried out by dissolving it in dilute nitric acid, adjusting the pH with a nitrate buffer, and titrating chelatometrically. Eriochrome black-T or a mixture of Eriochrome black-T with methyl-red or picric acid is a suitable indicator.[542]

Several colorimetric methods of determination and detection of azides have been developed. Most of these methods are based on the reaction of ferric ions with azide (*cf.* Mellor, VIII, 342). In particular, the original method which used ferric chloride and a dilute solution of azide ions has been developed quantitatively.[543] A modification involves distillation of the hydrogen azide into a ferric nitrate solution, adjustment to a definite volume and measurement of the transmission at 460 mμ against a ferric nitrate reference solution.[544] The use of ferric perchlorate is said to have the advantage that the lead and barium salts do not precipitate from the corresponding azide solution. In this case the transmission of the final solution, pH 2·2, is measured at 454 mμ.[545] The effects of acids, increased temperature, and foreign ions on the stability of the colour have been studied. It is claimed that 1–200 p.p.m. of azide ion could be determined with an accuracy of ~0·2%.[546] The absorption spectrum of the ferric azide complex has been widely studied,[152–4, 544–8] and a rapid method developed for the determination of hydrogen azide and ferric ions, either separately or simultaneously, in nitric acid containing hydrazine, ferrous ions, hydrogen azide, and ferric ions.[548] The method, which enables the rate of formation of hydrogen azide from hydrazine to be measured, involves measurement of the absorption and the nitric acid concentration. The optical density, d, is given by: $d = K[\mathrm{Fe}^{+++}][\mathrm{HN_3}]$. The parameter K involves the equilibrium constant of the reaction:

$$\mathrm{Fe}^{+++} + \mathrm{HN_3} \rightleftharpoons \mathrm{FeN_3}^{++} + \mathrm{H}^+$$

and is calculated from the known concentration of ferrous nitrate and sodium azide in nitric acid:

$$\log K = 3{\cdot}283 - 1{\cdot}361 \log [\mathrm{HNO_3}]$$

A colorimetric method has also been developed from the very rapid reaction of azide ions with nitrite ions in acidic solution.[246, 531] The concentration of unchanged nitrite ions is determined colorimetrically, *via* the diazotization of sulphanilic acid and coupling with α-naphthylamine. The method is suitable for solutions which are in the range 10^{-3} to 10^{-6} M. in azide.

The detection of hydrogen azide has been accomplished by the formation of both silver and ferric azides.[549]

In a manner analogous to the halides it has been found that the azide ion gives polarographically unsuitable mercury compounds on anodic dissolution at the dropping mercury electrode.[550] The half-wave potential is $+0{\cdot}20$ v. (becoming more negative with increasing concentration of azide), which is very similar to the $+0{\cdot}17$ v. found for the chloride ion, both values referring to 0·001 N. solution relative to the calomel electrode.[551] Nevertheless, satisfactory methods have been developed for the polarographic analysis of lead azide.[551–2] By taking advantage of the improvements in the polarography of halides produced by the presence of depolarizers which have a greater affinity for mercury ions, a more satisfactory procedure has been devised for the polarographic determination of azides.[553]

Various other established reactions of the azides have been used in further methods for the analysis of both azides and other substances. Thus, if equal volumes of a saturated solution of iodine in 1% aqueous potassium iodide and of 10% aqueous sodium azide in 1% starch are mixed and streaked on a chromatographic column, then the presence of a substance which catalyses the azide–iodine reaction, such as carbon disulphide, causes the blue colour to disappear.[554] Azide ions and trisodium pentacyanoammineferrate give a purple colour[159, 160] which turns yellow on the addition of hydrazine; the addition of a ketone or aldehyde restores the purple colour and so provides the basis of a method for the detection of these compounds.[555] Cobalt and some other transition metals can be detected by the formation of a characteristic colour when the acidified solution is treated with tributylamine and then an azide solution.[556] Cobalt can be determined by the measurement of the absorption at 540 mμ, pH 3·5–7·5, of the coloured solution produced when a cobalt solution is treated with 1% alcoholic dimethylglyoxime and 10% aqueous sodium azide in that order.[557] An extension of the facility with which colours can be obtained from cobalt compounds and azides is the development of a 'spot test' for sulphites.[558] Thus, a minimum of 0·5 μg. (dilution limit $1:10^5$) can be detected by the addition of a drop of the test solution to a filter paper which has been prepared by placing a drop of 1·5% $\mathrm{Co(NO_3)_2{,}6H_2O}$ solution at pH 5 and a drop of aqueous sodium azide on the paper. A positive result is the production of a light yellow colour which changes to blue on the addition of a drop of 0·2% *o*-tolidine in 2% acetic acid. The limits of the test and the influence of other ions have been studied.

The fast reaction of azides with nitrites enables nitrates and nitrites to be determined in the presence of each other. It has been found that the optimum concentration ratio is $[\mathrm{NaN_3}]/[\mathrm{NaNO_2}] = 3{\cdot}9$, and that increased acidity (sulphuric acid) may cause the decomposition of the nitrate and also result in the oxidation of nitrite to nitrate, which will lead to high analytical figures.[559]

In the determination of nitrites in the presence of large amounts of azide ion, interference by the latter can be avoided by precipitation as silver azide.[560] In the presence of sodium azide, and other substances which give rise to ammonia, the determination of ammonium salts is best accomplished by treatment with formaldehyde; the free acid thus liberated can be titrated directly.[561]

Sodium azide has been used as an internal standard in the quantitative determination of sodium fluoroacetate in dried residues from a soil dispersion, using infra-red spectrophotometry.[562] The intense absorption of the azide ion and the C—F bond means that extremely thin mulls containing a high proportion of Nujol are required.

Earlier reference to the use of azides, usually barium, in the preparation of discharge tubes has been made.[505–8] It has been shown that determination of the nitrogen content of the mirror deposit in such a tube indicates positively whether azides were used during manufacture.[563] Thus, if azides were not used then only 1–2 μg. nitrogen/tube is found; when azides have been used, however, the concentration is much higher.

ORGANIC CHEMISTRY OF THE INORGANIC AZIDES

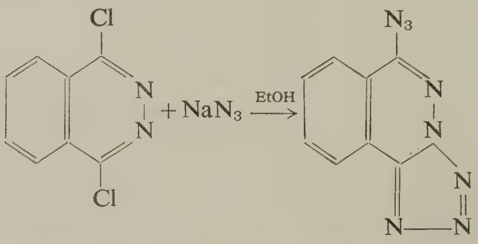
The azide group is a very reactive moiety. Hence, in addition to the many inorganic and organic reactions in which it resembles the halides, it enters into a large number of unique reactions.

The participation of hydrogen azide in the Schmidt reaction has already been discussed as also have several types of cyclization reactions (*vide* Hydrogen Azide). In addition the azide group can be inserted, unchanged, in organic molecules by a variety of substitution and addition reactions.

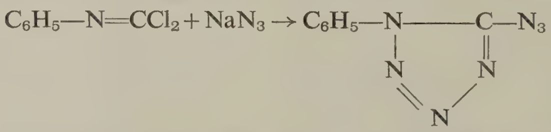
Substitution Reactions

REPLACEMENT OF HALOGEN

In this group lie halogen atoms attached to saturated carbon atoms, and activated halogens such as those in the acid chlorides etc. The nature of the remainder of the molecule frequently dictates the pattern of the reaction. For example, in a series of dichlorophthalazines,[564] dichloroquinazolines,[565–6] and dichloroquinoxalines[565] one of the chlorine atoms becomes replaced by an azido group whilst a tetrazole ring takes the place of the other, e.g.:



Similarly, phenylcarbylamine chloride undergoes replacement and cyclization[567]:



$$C_6H_5\text{—}N{=}CCl_2 + NaN_3 \rightarrow C_6H_5\text{—}N\text{———}C\text{—}N_3$$

α-Azidothioethers, R·S·CH$_2$N$_3$, where R = Me, C$_6$H$_5$, C$_6$H$_5$CH$_2$, are readily formed by the action of aqueous sodium azide on the corresponding chloride.[568] These compounds can be oxidized to the azidosulphones by monoperphthalic acid. Similarly 2:3-dichloro-*N*-phenylmaleimide gives the corresponding diazido compound with aqueous–ethanolic sodium azide.[569] Occasionally elimination occurs, e.g., menthyl chloride and either sodium or silver azide afford menthene; on the other hand vigorous conditions are required to produce an azide from 2-chloro*cyclo*hexanol, and even then it is the azidohydrin of *cyclo*hexene.[570]

Refs. p. 58

$\alpha:\omega$-Dibromo-alkanes when refluxed with sodium azide in aqueous methanol give high yields of the diazides.[571] The same procedure also succeeds with sulphonyl esters, chloromethyl aromatic compounds, bis-ω-iodoalkyl ethers, and bis-ω-chloroalkyl amines. Ethyl α-bromo-β-ethoxypropionate gives the corresponding azide in good yield when heated with aqueous ethanolic sodium azide,[572] as does β-phenylethyl bromide.[573] Diethyl bromomalonate, however, undergoes a disproportionation reaction thus[574]:

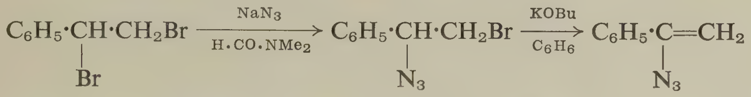
$$2BrCH(COOEt)_2 + 2NaN_3 \rightarrow CH_2(COOEt)_2 + (N_3)_2C(COOEt)_2 + 2NaBr$$

Sodium azide in acetone reacts normally with 11-bromo-undec-1-yne to give a high yield of the acetylenic azide.[575]

Aryl-α-azidoketones, $R.CO.CH_2N_3$, are prepared in an straightforward manner from the bromide and aqueous–alcoholic sodium azide.[576–9] The presence of a carboxyl group or methoxycarbonyl *ortho* to the ketone completely inhibits the reaction.[579]

α-Acetoazido sugars are best prepared by the action of silver azide in anhydrous ether on the corresponding α-acetobromo sugar.[580]

The action of sodium azide in formdimethylamide on styrene dibromide resulted in the replacement of only one bromine atom and the azide group is stable towards potassium *tert.*-butoxide in benzene.[581]



$$C_6H_5{\cdot}\underset{\displaystyle Br}{\underset{|}{CH}}{\cdot}CH_2Br \xrightarrow[H.CO.NMe_2]{NaN_3} C_6H_5{\cdot}\underset{\displaystyle N_3}{\underset{|}{CH}}{\cdot}CH_2Br \xrightarrow[C_6H_6]{KOBu} C_6H_5{\cdot}\underset{\displaystyle N_3}{\underset{|}{C}}{=}CH_2$$

The replacement reactions of the azide group have been widely studied by kinetic methods and also from a configurational aspect. Thus, it has been shown that the azido group attached to a benzene nucleus lies midway between methyl and methoxy groups in its effect on electrophilic aromatic substitution and about the same as fluoride in its acid strengthening effect.[582] The reactions of tetraethylammonium salts such as chloride, bromide, and azide with diphenylmethyl bromide in nitromethane have been studied.[583] The second-order components for substitution by azide and bromide were in the ratio 128:1, and for azide and chloride 1900:1. The relative capacities for the capture of $(C_6H_5)_2{\cdot}CH^+$ were: azide ~ 5, chloride $\sim 2{\cdot}86$, and bromide $\sim 1{\cdot}0$. A wide series of configurationally related azides has been prepared by the action of sodium azide on the iodides and their optical rotations have been compared.[584] Inversion of configuration occurs in the reaction between sodium azide and $(+)$-$CH_3CH(Br)CO_2H$, and the azide produced can be reduced to (D)-alanine with retention of configuration.[585] This reaction sequence completed the genetic chain between the configurational standards used for the comparison of sugars and amino acids. The role of azides in the solvolysis of tertiary chlorides etc. has been widely examined.[586–9]

Acid chlorides react smoothly and rapidly with pure sodium azide. It has been found that commercial sodium azide, manufactured by the sodamide–nitrous oxide route, is not as effective as that prepared via the hydrazine–alkyl nitrite route.[590–3] It has been shown that if this commercial product is rubbed with a trace of hydrazine hydrate and precipitated from water with the aid of acetone, then the product is even more reactive than the purest material obtained from hydrazine and alkyl nitrite.[593]

This method of preparing acid azides is very widely used.[594–8] The presence of a tertiary amine or amine salt is said to be advantageous,[599] but if the acid is unstable in the presence of mineral acids then impure acid chlorides and hence impure azides result. For such cases an alternative method has been devised in which sodium azide reacts with mixed anhydrides to yield the acid azides in excellent yields under mild conditions.[600]

An intimate mixture of sodium azide, potassium hydroxide, and benzoyl chloride reacts spontaneously with evolution of heat and the formation of $(C_6H_5{\cdot}NH)_2CO$ as the main product.[601]

In addition to the azides derived from carboxylic acid chlorides sodium azide also converts sulphonyl chlorides into sulphonyl azides,[602] and organophosphorus chlorides, $(R_2N)_2P(O)Cl$, into the corresponding azides.[96, 603]

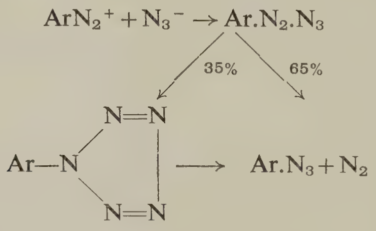
The well known activity of the chloro-substituents in polynitrochlorobenzenes enables, for example, picryl azide to be produced quantitatively at room temperature; 2:4-dinitro-1:3:5-trichlorobenzene reacts with sodium azide in boiling aqueous acetone–alcohol mixture to give 2:4-dinitro-1:3:5-triazidobenzene.[604]

REPLACEMENT OF HYDROXYL

In the presence of trichloracetic acid hydrogen azide converts substituted benzhydryl alcohols into the benzhydryl azide.[605]

REPLACEMENT OF DIAZONIUM

The conversion of the diazonium group into an azido group by the action of sodium azide is well established and has been examined with the aid of [^{15}N]nitrogen.[606–611] The reaction has been demonstrated to be two-stage: first, the azide ion rapidly adds to the diazonium ion giving a benzene diazoazide, and this compound then decomposes by two routes:



This reaction is convenient and frequently gives very high yields. It provides for the preparation of compounds such as 2-azidodiphenyl and its derivatives,[612] 2-azidodiphenyl ether and sulphide, 2:2′-diazidodiphenyl, 2-azidobenzophenone,[613] and 1:4-diazidobenzene,[614] etc. New initiating explosives have also been made by this method, namely, the lead salts of 4:6-dinitro-2-azidophenol, 2:6-dinitro-4-azido-*m*-cresol, and 3-azido-5-nitro-salicylic acid.[615]

REPLACEMENT OF SULPHONATE ESTER

The nucleophilic substitution of the *p*-toluenesulphonate group ('tosylate') by azide ion in aprotic solvents has been studied in the steroid field. As an example, a yield of 92% of the C-17α-azide from testosterone tosylate was obtained in *N*-methylpyrrolidone–*tert.*-butanol, compared with only 43% in formdimethylamide.[616] The displacement of a secondary methanesulphonate group in a sugar molecule by means of sodium azide in formdimethylamide provided the first step in an aminosugar synthesis.[617]

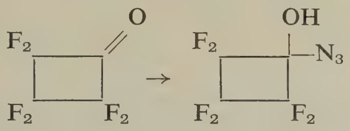
Addition Reactions

TO CARBON–CARBON DOUBLE BONDS

In the presence of an acidic catalyst hydrogen azide adds to alkenes, cyclic alkenes, arylalkenes, and *cyclo*alkylalkenes to form azides; thus, an excess of propylene reacts with hydrogen azide in the presence of solid phosphoric acid at 150° to yield *iso*-propyl azide.[618] In the presence of acetic acid hydrogen azide adds to conjugated unsaturated compounds, sometimes very rapidly and in good yields, *e.g.*, ω-nitrostyrene gives α-azido-ω-nitro-ethylbenzene in 69% yield.[619] Trichloroacetic acid has been used to catalyse the addition of hydrogen azide to 1:1-diarylethylenes.[605]

TO CARBONYL COMPOUNDS

The addition of hydrogen azide to perfluoro*cyclo*butanone affords what is said to be the first stable azido-alcohol[620]:

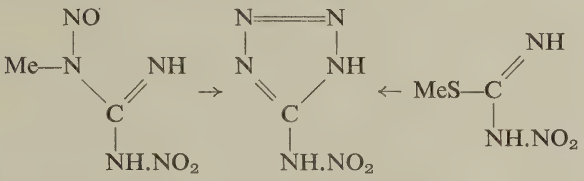


TO EPOXIDES

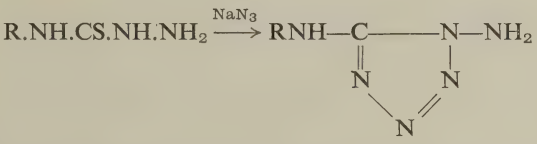
Epoxides react with sodium azide in the presence of perchlorate ion at pH 6–9 to give azido-alcohols in good yields.[621]

Miscellaneous

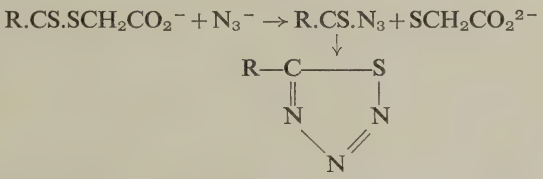
The reaction of sodium azide with either *N*-methyl-*N*-nitroso-*N*′-nitro-guanidine or *N*-nitro-*S*-methyl*iso*thiourea gives 5-nitroaminotetrazole[622]:



5-Oxazolones, when treated with sodium azide in tetrahydrofuran followed by aluminium chloride in tetrahydrofuran, undergo ring-cleavage and ring-closure to form tetrazoles.[623] Sodium azide and lead monoxide react with substituted thiosemicarbazides with elimination of sulphur and the formation of 5-substituted 1-aminotetrazoles[624]:



Carboxymethyldithioates react with sodium azide with the formation of a thioazide which is converted into a 1:2:3:4-thiatriazole[625]:


$$R.CS.SCH_2CO_2^- + N_3^- \rightarrow R.CS.N_3 + SCH_2CO_2^{2-}$$

Alkali metal azides in water react with chlorinated lactones to form azidolactones which are useful for the production of cellular synthetic rubber.[626]

The decomposition of 1-hydroxy*cyclo*hexyl peroxide with ferrous sulphate in the presence of an alkali metal azide gives ω-azidohexanoic acid, $N_3 \cdot (CH_2)_5CO_2H$.[627]

Benzyl azide is strikingly stable towards hydrolytic reactions in contrast to the benzyl halides. This stability has been shown to be chiefly connected with an increase in the bond order of the azidomethyl group,[628] and spectroscopic studies established that this is associated with the shortening of the C—N bond length between the methyl carbon atom and the azido nitrogen atom to which it is attached.[629] For benzyl azide, calculation of the energy of the hyperconjugative interaction between the methylene and azido groups has shown that the hyperconjugation is stronger between the methylene and the azido groups than between the methylene and the phenyl groups.[630] The strength of the hyperconjugation suggests that it is related to the marked stability towards alkaline hydrolysis of molecules containing the azidomethyl group bonded to a carbon chain.

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SECTION XX

HYDRAZINE

BY G. H. HUDSON, R. C. H. SPENCER AND (MRS.) J. P. STERN

In the last twenty-five years hydrazine (diamide) has developed from being a versatile laboratory reagent into an important industrial chemical, the annual world production of which is now well over 3000 tons. The renewed interest in hydrazine arose from the German discovery of its suitability for use in conjunction with an appropriate oxidant as a rocket fuel during the 1939–1945 war. The availability of hydrazine has, in turn, stimulated its further investigation and its utilization.

PRODUCTION

The Raschig Synthesis

The I.G. Farbenindustrie process[1] was based on the original Raschig preparation (Mellor, VIII, 309) which remains the most economical synthesis of hydrazine. Ammonia is partly oxidized by sodium hypochlorite in slightly alkaline aqueous solution with the intermediate formation of chloramine which reacts with excess of ammonia forming hydrazine.

$$NH_2 + OCl^- \rightarrow NH_2Cl + OH^- \qquad (1)$$

$$NH_2Cl + NH_3 + OH^- \rightarrow N_2H_4 + Cl^- + H_2O \qquad (2)$$

Raschig had originally shown that reaction (2) is slow and competes with reaction (3), below, which is catalysed by metals and threatens the yield of hydrazine.

$$2NH_2Cl + N_2H_4 \rightarrow 2NH_4Cl + N_2 \qquad (3)$$

The presence of trace metal catalysts, notably copper, has[2] a detrimental effect on the hydrazine yield and, if very pure reagents and triply distilled water are used in carefully cleaned reaction vessels, high yields are possible.[3] The copper content of ordinary water (1 p.p.m.) makes the use of an inhibitor necessary. In the uninhibited reaction,[4] reaction (3) is about eighteen times as fast as reaction (2) at 80–90°C. [Joyner's temperatures (Mellor, VIII, 309)] and the success of the preparation depends on the rate at which reaction (2) may be made to occur. Reaction (2) has the higher temperature coefficient[1] and can be promoted over (3) by rapid heating of the cold chloramine solution. Reaction (1) is very fast and goes to completion even in the cold.

A wide range of inhibitors has been examined[5]; effective inhibition is provided by three distinct types of agents:

- (*a*) Copper-complexing agents, such as high molecular-weight proteins, some amino-acids and some of the more effective polydentate chelating agents.
- (*b*) Hydrophilic colloids such as commercially available polysaccharide polymers and their derivatives.
- (*c*) Co-precipitating agents, *e.g.*, magnesium sulphate, by entrapment within a precipitate or colloidal dispersion.

These all inactivate copper and other metal ions in the solution and prevent catalysis of reaction (3). Few of these materials, however, are as efficient as very pure gelatin.

From experiments with *tert.*-butyl hypochlorite it appears[6] that only in alkaline solution does chloramine react with ammonia to give hydrazine in high yield. Sufficient free alkali is normally present in commercial sodium hypochlorite.

Joyner's discoveries (Mellor, VIII, 309) that increasing the ammonia:hypochlorite ratio increases the yield of hydrazine and that the yield depends on the amount of glue added, when this is present in small quantities, have been further investigated by Reed[7] and co-workers, whose results for the uncatalysed and catalysed reactions are shown in Figures 1 and 2 respectively. The results were obtained in a continuous system over a range of temperatures.

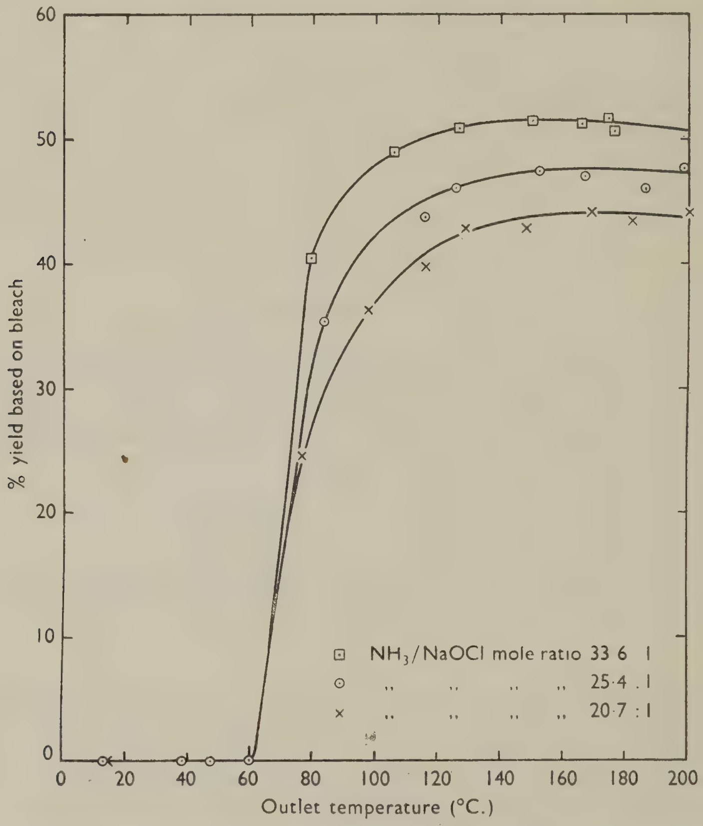


FIG. 1.—Relationship between temperature and hydrazine yield for different ammonia/bleach ratios

The most striking effect of the addition of the catalyst is to improve the hydrazine yield at temperatures below 60°C., below which none is formed in the absence of inhibitor. The curve of yield of hydrazine flattens off with increasing NH_3/OCl^- mole ratio above about 30, and the use of ratios much above this in an industrial process involves the expensive recycling of large quantities of unconverted ammonia. At low ammonia concentrations, chloramine loss is likely to occur through the side reaction:

$$3NH_2Cl + 3OH^- \rightarrow N_2 + NH_3 + 3Cl^- + 3H_2O \qquad (4)$$

Chloramine may under varying conditions be destroyed in other side reactions and these have been discussed in detail.[8]

The modern Raschig manufacturing process[1, 9] is continuous and involves mixing of the hypochlorite and ammonia solutions in the cold, followed by rapid heating to 150–180°C. under pressure in order to prevent loss of ammonia. Ammonia gas is absorbed in water to form a 25% w/w solution and 10–20% glue solution is added continuously. This solution is then continuously mixed in the cold with water and a solution of sodium hypochlorite containing 7% of available chlorine so that the final reaction mixture has an NH_3/OCl^- mole ratio of 30. The liquid is compressed to 150 lb./sq. in. and admitted to the reactor which consists of a steam-jacketed bank of stainless-steel tubes in parallel.

With an outlet temperature of about 150°C. and a residence time of 1 sec. the liquid contains at this stage 0·5–0·7 wt.-% of hydrazine, corresponding to a 60–65% conversion based on hypochlorite. It then passes to an atmospheric reducing valve where two-thirds of the ammonia and some steam flash off into two expansion towers and are scrubbed with aqueous ammonia to extract traces of hydrazine. The main liquid stream, together with the residues from the towers, is stripped of ammonia and of some steam in a mild-steel stripping column which concentrates the liquid to 2% of hydrazine. The ammoniacal vapours from the stripper are condensed in a tubular, water-cooled condenser and the condensate is pumped to the head of a second column which acts as a falling film absorber for the ammonia from the two expansion towers. Make-up ammonia is metered in to maintain the output from the condensers at 25% w/w ammonia for recycling in the reaction mixture.

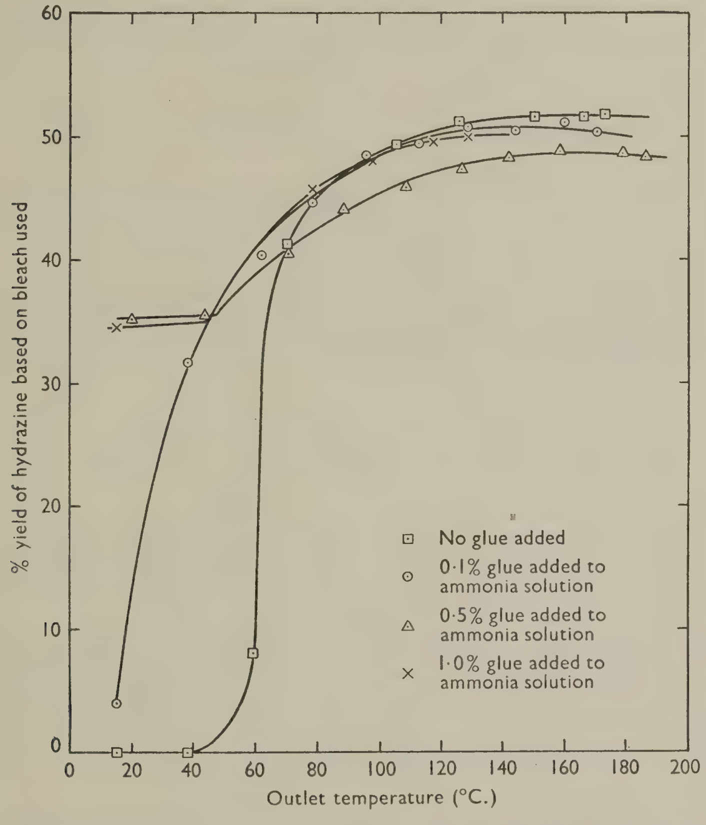


FIG. 2.—Effect of increasing amounts of glue on the yield of hydrazine

The stripping column bottoms are freed from salt in a forced circulation stainless-steel evaporator from which the salt containing a little ammonium chloride is continuously separated by centrifugal action. The vapour from the evaporator is further freed from water in a column giving a 10% hydrazine solution as the bottoms product. This solution may be concentrated further by one or more distillation stages and is usually finally obtained as pure hydrazine hydrate N_2H_4,H_2O (equivalent to 64% of hydrazine), *i.e.*, close to the constant-boiling composition of the hydrazine–water system.

The Raschig synthesis may be varied by use of ammonia derivatives such as urea[10] or biuret[11] and the process has been operated commercially with urea in Germany and America. Yields up to 70% are reported, the overall reaction being:

$$NH_2.CO.NH_2 + OCl^- + 2OH^- \rightarrow N_2H_4 + Cl^- + CO_3^{2-} + H_2O$$

The same inhibitors are necessary and yields are similarly improved by rapid heating of the reaction mixture.

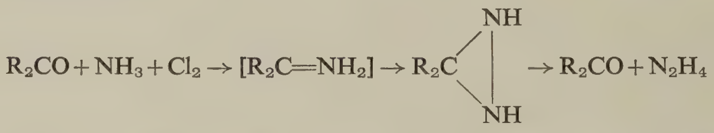
N-Substituted hydrazines may also be readily prepared[12] by the action of chloramine on primary and secondary amines under similar conditions. For example, unsymmetrical dimethylhydrazine may be prepared from chloramine and dimethylamine:

$$(CH_3)_2NH + Cl.NH_2 + OH^- \rightarrow (CH_3)_2N.NH_2 + Cl^- + H_2O$$

a process which is also operated commercially.

Audrieth *et al.* have shown[13] that the reaction may be further generalized by the use of *N*-chloro compounds other than chloramine, e.g., *N*-chlorosuccinimide, which gives hydrazine on reaction with ammonia.

A newer variation[14, 15] of the Raschig synthesis involves the interaction of chlorine and anhydrous ammonia (in excess) in presence of a ketone, when a diaza*cyclo*propane (*iso*hydrazone) is formed as intermediate. Acidic hydrolysis then regenerates the ketone:



and yields hydrazine, usually isolated as the sulphate. The reaction is successful both in the liquid[14] and in the vapour phase.[15] The N–N bond appears to be formed by addition of chloramine to the Schiff's base (imine) derived from the carbonyl compound and ammonia (or primary amines).[16]

The use of anhydrous ammonia has also been investigated[17] as a means of avoiding the costly concentration stages of the conventional Raschig process; yields of about 30% are obtained when chlorine is introduced into a liquid ammonia stream either directly or as a solution in carbon tetrachloride. A very large excess of ammonia (about 300:1) is necessary and this makes the process unattractive commercially.

PREPARATION OF ANHYDROUS HYDRAZINE

Anhydrous hydrazine may be conveniently obtained in several ways from the solutions near the constant boiling composition produced by the normal Raschig manufacture. One method[18] requires counter-current contacting at 120 mm. Hg and 75°C. of the boiling aqueous hydrazine solution with an equivalent amount of sodium hydroxide and subsequent fractionation at atmospheric pressure. In this way a product containing at least 95% of hydrazine may be conveniently obtained. Calcium oxide and barium oxide have also been used in the later stages of concentration, but the heterogeneous mixture is not ideal for distillation. In all distillations care must be taken to avoid thermal and catalytic decomposition and to exclude oxygen with which hydrazine forms explosive mixtures. It is best to distil under reduced pressure or in an atmosphere of nitrogen; further butane and cadmium oxide have been claimed[19] to act as stabilizers.

Azeotropic or extractive distillation procedures using xylenes, aniline, *n*-hexyl alcohol, pyridine or glycols as third components have been described.[20] It is claimed[21] that 96% hydrazine may be obtained without explosion risk by distillation at atm. pressure of an aqueous solution with sodium hydroxide and a saturated aliphatic hydrocarbon of b.p. 90–150°C.; 99% of the hydrazine may be recovered by separation of the non-organic layer of the fraction b.p. 103·5–107°C./760 mm.

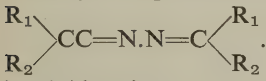
Another useful method[22] involves the isolation of the sparingly soluble mono-hydrazine sulphate, N_2H_4,H_2SO_4, by precipitation in the cold with sulphuric acid. The sulphate is further treated with liquid or gaseous ammonia and hydrazine is formed by the ammonolysis:

$$N_2H_4.H_2SO_4 + 2NH_3 \rightarrow N_2H_4 + (NH_4)_2SO_4$$

Removal of the insoluble ammonium sulphate allows complete separation of ammonia by evaporation at 0°C., leaving anhydrous hydrazine. Other salts, e.g., the hydrochloride,[23] may be used. Analogously, hydrazine hydrate may be prepared on the small scale[24] without cumbersome fractionation.

A phase equilibrium study[25] of the N_2H_4–H_2O–NaOH system showed that a system of 85% hydrazine hydrate containing molar equivalents of sodium hydroxide and water separates into two phases at temperatures above 60°C. At 70°C. the upper, hydrazine-rich, layer contains 90% of hydrazine in 80% yield. Anhydrous hydrazine is then readily obtained by distillation under reduced pressure.

Numerous other procedures have been described and include fractional crystallization of concentrated hydrazine solutions[26]; this method is unsuitable for dilute solutions since very low temperatures are necessary. Use of alkali or alkaline-earth metals dissolved in liquid ammonia has been reported,[27] but the method is potentially hazardous owing to the possibility of formation of an explosive metal hydrazide. A procedure[28] by which 63% hydrazine solution is agitated with quick-lime in an atmosphere of hydrogen for 24 hours, after which a stream of hydrogen is passed through the cooled mixture and the anhydrous N_2H_4 condensed from the gas stream, is thought to be safer.

Dilute hydrazine solutions may be worked up by exploitation of the reaction of carbonyl compounds with hydrazine to form[29] hydrazones or azines of the type  $(R_1)(R_2)CC{=}N.N{=}C(R_1)(R_2)$. Certain aromatic aldehydes, e.g., benzaldehyde, form insoluble azines:

$$2C_6H_5CHO + N_2H_4 \rightarrow C_6H_5{=}N.N{=}CH.C_6H_5$$

These may be separated and the carbonyl compound recovered by acid hydrolysis. Alternatively[30] acetone may be added to dilute hydrazine solutions and a series of extractive distillations then permits the preparation of concentrated solutions of hydrazine, suitable for further drying.

Other Methods of Preparing Hydrazine

Developments of the Raschig manufacturing process have been directed mainly at conserving steam, but only marginal savings can thus be hoped for and the present relatively high cost of hydrazine has stimulated examination of many possible synthetic routes. Although a very large number of preparations has been reported in the technical and patent literature, all fall into one or other of three groups.

PARTIAL OXIDATION OF AMMONIA OR AMMONIA DERIVATIVES

The direct oxidation of ammonia with molecular oxygen yielding traces of hydrazine, first noted by Raschig (Mellor, VIII, 309) has been confirmed[31]: traces of hydrazine were identified when ammonia and a little oxygen were passed rapidly over an alkaline surface, activated with metal oxides, and immediately quenched. A recent patent describes[32] the preparation of hydrazine by passing a preheated stream of ammonia into a high-temperature hydrogen/oxygen flame from which a 2·25 wt.-% aqueous solution of hydrazine may be condensed. Traces of hydrazine were also reported[33] when mixtures of ammonia and oxygen were passed over a heated platinum catalyst at low pressure (0·01 mm. Hg) into a vessel surrounded by liquid air. The passage of an oxygen/ammonia stream through an ozonizer at low temperatures,[34] followed by rapid removal of the hydrazine formed by spraying a liquid paraffin hydrocarbon into the reaction chamber, is claimed to give fair yields.

Oxidizing agents such as nitrous oxide, silver oxide and fluorine also produce[35] trace amounts of hydrazine, although the more complete oxidation to nitrogen is favoured thermodynamically.

A related method of preparation[36] is the reduction of nitrous oxide by excess of hydrogen in presence of ammonia over metal catalysts at temperatures up to 400°C.

THE DECOMPOSITION OF AMMONIA AND RELATED COMPOUNDS

Considerable attention has been focussed on methods of splitting ammonia, presumably into NH_2^- radicals which re-form to hydrazine. Photolytic fission, both unsensitized at 1849 A. and mercury-photosensitized at 1849 A. and 2537 A., at normal pressures and low temperature, gives[37] appreciably better yields in flow systems; in the unsensitized photolysis yields may then be as high as 90%, based on ammonia decomposition. The sensitized decomposition is less efficient owing to the preferential photosensitized decomposition of hydrazine. The presence of a H atom acceptor, such as an olefine, improves the yield in terms of ammonia decomposed, but this is usually a very small fraction (< 1%) of the total ammonia exposed to photolysis.

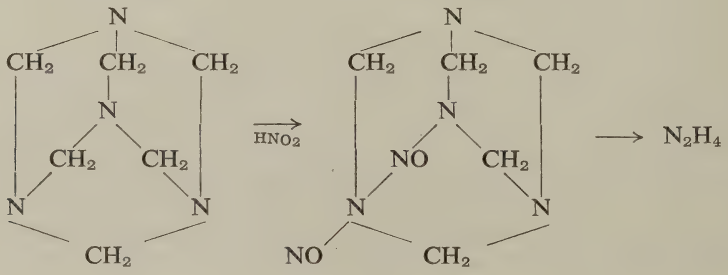
Hydrazine is also formed in the decomposition of ammonia gas in an electrical discharge,[38] a process which has been examined as a possible mode of industrial manufacture: the reaction is favoured at low pressure (5–10 mm. Hg). One patent describes a procedure in a platinum coated chamber (to remove H atoms by recombination).

Yet another method by which ammonia may be decomposed utilizes a gaseous glow discharge.[39] Alternatively an electrical discharge is maintained between a solution of ammonium nitrate in liquid ammonia at −80°C. under reduced pressure and a platinum anode just above the liquid surface; a hydrazine yield of 2·5 moles per Faraday has been reported.[40]

Hydrazine is formed[41] by thermal action on an incandescent filament immersed in liquid ammonia and, very recently, hydrazine formation has been proposed[42] by 'fissio-chemical' reaction. Liquid ammonia containing a fissile material, e.g. uranium oxide, is split into ions by the uranium oxide fission fragments having energies of 10^8 ev. The hydrazine formed from the ions is very rapidly quenched and stabilized by the bulk of the liquid. Hydrazine formation in small yield by electron bombardment of ammonia has also been reported.[43]

FROM LARGER NITROGEN-CONTAINING MOLECULES

Hydrazine is formed in the reduction of a variety of nitrogen-containing bodies. Thus nitrourea, $NH_2.CO.NH.NO_2$, and nitroguanidine, $NH_2.C(:NH).NH.NO_2$ are reduced to the corresponding hydrazine derivatives, semicarbazide and aminoguanidine, which readily yield hydrazine on hydrolysis. The condensation product of formaldehyde and ammonia, hexamethylenetetramine, on nitrosation yields dinitrosopentamethylenetetramine which gives hydrazine under reducing conditions,[44]



The controlled reduction of hydrazoic acid or azides also produces traces of hydrazine.[45] If the reaction medium contains sulphuric acid so that the hydrazine is precipitated as its sulphate, the yields are reported to be greater.

Hydrazine is also formed from urea when it is heated with carbonyl-forming metals, e.g., nickel and iron.[46] The reaction with nickel goes most readily and may be carried out at 60–70°C. The overall reaction is:

$$CO(NH_2)_2 \rightarrow CO + N_2H_4$$

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THE PHYSICAL PROPERTIES OF HYDRAZINE

ANHYDROUS HYDRAZINE

Anhydrous hydrazine at normal temperature is a colourless liquid which fumes in air and has a smell similar to, but less pungent than, that of ammonia. Recent melting point determinations give values between 1° and 2°C.[1, 2, 3]; the most recent value, due to Mohr and Audrieth,[4] of 2·0° is the highest recorded and now generally accepted as correct. Two recent workers have independently carried out boiling point determinations and give values of 113·4°C.[1] and 113·5°C.[5] at 760 mm. pressure which are in agreement with the values previously reported (Mellor, VIII, 311). Values of 3025 g.-cal./mol.[3] and of between 9600 and 10,700[3, 5, 6, 7] with a calculated value of 9760 g.-cal./mol. for the latent heat of fusion and the latent heat of vaporization of hydrazine, respectively, have been reported. Vapour pressure curves for liquid hydrazine have been prepared between 20·21° and 114·15°C. by Hieber and Woerner,[6] and between 0° and 70°C. by Scott and his co-workers whose figures fit the Antoine equation:

$$\log_{10} P\,(\text{mm.}) = 7{\cdot}80687 - \frac{1680{\cdot}745}{t(^\circ\text{C.}) + 227{\cdot}74}$$

In the vapour phase between 140° and 380°C. the vapour pressure has been measured by de Bruyn[8] whose results fit the equation:

$$\log_{10} P\,(\text{mm.}) = 9{\cdot}40 - \frac{2814{\cdot}9}{T(^\circ\text{K.})} - 0{\cdot}006931T + 0{\cdot}000003746T^2$$

Trouton's constant calculated from the above equation and the calculated latent heat of vaporization (9760 g.-cal./mol.) is 25·23 g.-cal./mol. degree, which is higher than that for an unassociated liquid and therefore indicates that liquid hydrazine is to some extent associated. The critical constants due to de Bruyn (Mellor, VIII, 311) are now in doubt in view of the known thermal instability of hydrazine at such temperatures. The density of liquid hydrazine is best represented by the equation[9]:

$$\rho = 1{\cdot}0253(1 - 0{\cdot}00085t)$$

where t is the temperature in °C. This corresponds to a value of 1·0126 g./c.c. at 15°C., equivalent to a density relative to water at 15°C. of 1·0140, in agreement with de Bruyn's original value (Mellor, VIII, 311); the density of the solid at −5°C. has been reported to be 1·146 g./c.c.[10] The viscosity of liquid hydrazine has been measured between 0° and 80°C. and does not differ greatly from that of water.[1, 9, 11]

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The surface tension has been reported to be 66·67[12] and 62·32[13] dyne cm.$^{-1}$ at 25 and 35°C. respectively, the parachor is 90·7,[13] and the refractive index at 35° for the sodium D-line is 1·46444.[13]

In view of the importance of hydrazine as a rocket fuel much work has been done on its thermochemistry[3, 14, 15] and Audrieth[16] has recalculated some of the more important thermodynamic parameters; these are reproduced in Table I.

Table I.—Thermodynamic Properties of Hydrazine[16]

Temp. (°K.)	Entropy (g.-cal./mole °C.)	Enthalpy (g.-cal./mole)	Heat of formation (g.-cal./mole)	Free energy of formation of gaseous hydrazine (g.-cal./mole)
298·16	57·01	44,780	22,700	37,960
500	64·65	47,800	21,500	48,670
1000	78·26	57,770	20,660	76,340
1500	87·97	69,810	21,190	104,090

In addition the heat of combustion is given as 148,635 g.-cal./mol., and the heat of solution (hydration) as 3893 g.-cal./mole.[15] Heat capacities for solid,[3] liquid[3] and gaseous[37, 17] hydrazine have also been determined; in the solid and gaseous states these values vary widely with temperature, but in the liquid state they vary only between 23·29 g.-cal./mole°C. at 274·69°K. and 24·34 g.-cal./mole°C. at 340°K.

The electrical properties of hydrazine, too, are of some importance. Recent determinations of the dielectric constant,[18] 58·5 at 0°C. and 51·7 at 25°C., are in good agreement with figures originally quoted (Mellor, VIII, 311); this constant and the low specific conductivity,[9] $1{\cdot}1\text{–}2{\cdot}0 \times 10^{-6}$ ohm^{-1} at 0°C. and $2{\cdot}3\text{–}2{\cdot}8 \times 10^{-6}$ ohm^{-1} at 25°C., indicate its excellence as an electrolytic solvent. Liquid hydrazine undergoes slight self-ionization according to the equation:

$$2N_2H_4 \rightleftharpoons N_2H_5^+ + NH_3^-$$

with an ionic product calculated[2] to be of the order of 2×10^{-25}, which is much larger than the corresponding value for liquid ammonia (10^{-33}). The dipole moment of hydrazine has been measured[19] and reported as $1{\cdot}83\text{–}1{\cdot}85 \times 10^{-18}$ e.s.u., which compares well with a value of $1{\cdot}70 \times 10^{-18}$ e.s.u. calculated for a *cis*-form of hydrazine in which there is restricted rotation about the N–N bond.[20] Such a structure is supported by electron diffraction measurements which indicate also that hydrazine is not associated in the vapour phase. The structure of solid hydrazine has also been studied[21, 22]; it forms monoclinic crystals, has two N_2H_4 molecules to the unit cell, which has the dimensions $a = 3{\cdot}56$, $b = 5{\cdot}78$, $c = 4{\cdot}53$ A. and $\beta = 109{\cdot}5°$, and the N–N bond distance is 1·46 A.

AQUEOUS HYDRAZINE

The concentrations of aqueous hydrazine solutions are often given in terms of hydrazine hydrate concentration, evidence for the existence of which comes from studies of physical properties of hydrazine solutions which show anomalies at about 50 mol. per cent of hydrazine. Freezing point determinations[1, 4, 23] indicate the existence of a monohydrate, N_2H_4,H_2O, as a solid phase melting at −51·7°C. and two eutectics corresponding to compositions of approximately $N_2H_4,2H_2O$ and $2N_2H_4,H_2O$ with melting points of −54°C. and less than −76°C., respectively. Other physical properties supporting the existence of a monohydrate include the viscosity and density,[1, 24] which pass through a maximum at 50 molar-% of hydrazine, and the parachor,[12] which passes through a minimum at the same point. The surface tension reaches a maximum of 75·47 dyne cm.$^{-1}$ at about 30–35 molar-% of hydrazine,[12] roughly corresponding to the dihydrate $N_2H_4,2H_2O$, but evidence for the existence of this compound is by no means conclusive. Improvements in technique and apparatus have permitted the re-examination of the vapour–liquid equilibrium in the hydrazine–water system[25–27]; the maximum boiling-point azeotrope boils at 120·1° and has a composition of 70 wt.-% of hydrazine, roughly corresponding to a compound $2N_2H_4,H_2O$.

Values for the equilibrium constant and thermodynamic constants for the gaseous equilibrium $N_2H_4,H_2O \rightleftharpoons N_2H_4 + H_2O$ are given[28]; $\log_{10} K_{\text{atm.}} = \frac{3054}{T} + 8{\cdot}55$; $\Delta H^\circ_{298} = 13{\cdot}97 \pm 0{\cdot}10$ kcal./mol., $\Delta S^\circ_{298} = 39{\cdot}1 \pm 0{\cdot}4$ g.-cal./mole degree; the entropy of N_2H_4,H_2O vapour = 63·4 g.-cal./mole degree and heat of formation of N_2H_4,H_2O at 298°K. = −49·02 kcal./mole, thus confirming the small degree of association of hydrazine and water in the gas phase.[29] Equilibrium compositions are also given for a vapour–liquid equilibrium at constant pressures between 124·8 and 700·6 mm. Hg.[30] The velocity of sound in hydrazine–water mixtures over the range 0–100% has been measured by means of the Debye–Sears ultrasonic light diffraction phenomenon[31]; the velocity of sound in hydrazine is higher than for any other liquid hitherto examined and with the aqueous mixtures a smooth curve was obtained showing no discontinuities corresponding to the discontinuities in the freezing point curves.

The electrical properties of hydrazine hydrate have also been studied and dissociation constants have been measured. An early determination, using Haber's glass cell,[32] gives a value of $1{\cdot}4 \times 10^{-6}$, close to that obtained by measurements of the solubility of hydrazine picrate[33] in various salt solutions ($1{\cdot}5 \times 10^{-6}$), but later papers[34, 35, 36] record the following values:

$$\frac{[N_2H_5^+][OH^-]}{[N_2H_4]} = 8{\cdot}5 \times 10^{-7},\ 8{\cdot}63 \times 10^{-7},\ \text{and}\ 9 \times 10^{-7}$$

$$\frac{[N_2H_6^{2+}][OH^-]}{[N_2H_5^+]} = 8{\cdot}9 \times 10^{-16}\ \text{and}\ 1{\cdot}86 \times 10^{-14}$$

Systems containing Hydrazine

TERNARY SYSTEMS OF HYDRAZINE AND WATER

Addition of sodium hydroxide to aqueous hydrazine results in the separation of the system into two liquid phases; the lighter phase at 100°C. contains hydrazine 92·7%, sodium hydroxide 2·4%, and water 4·9%.[37] This simple salting-out procedure affords a convenient method of concentrating dilute hydrazine solutions.[4] The salts examined include potassium carbonate, potassium hydroxide, sodium carbonate, sodium phosphate, and sodium sulphate, but only sodium hydroxide was effective. Other ternary hydrazine–water systems examined include those with sodium carbonate and with glycerol.[38]

HYDRAZINE–AMMONIA

The pressure–temperature–composition curve of the system hydrazine–ammonia has been determined up to the critical curve[39] and no evidence was found for the formation of compounds or mixed crystals, although in the presence of traces of water formation of mixed crystals may occur. A study of the liquid–vapour equilibrium of the system[40] suggests, however, that molecular association of hydrazine in liquid ammonia solution may occur.

THE TERNARY SYSTEM HYDRAZINE–AMMONIA–HYDROCHLORIC ACID

This system has also been examined and the solid–liquid equilibrium established in the portion of the diagram corresponding to hydrazine–ammonia–ammonium chloride at pressures near 1 atmosphere. The conditions for removal of ammonium chloride from the system by crystallization are given and a ternary compound of unconfirmed composition, but thought to be N_2H_4,HCl,NH_3, having a melting point of −25°, has been detected.[41]

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OTHER BINARY SYSTEMS

Examination of the system hydrazine–methanol shows the existence of compounds N_2H_4,CH_3OH, m.p. −47·3°, $N_2H_4,2CH_3OH$, m.p. −57·8°, and $N_2H_4,4CH_3OH$, m.p. −69·5°, while in the hydrazine–ethanol system the compound $N_2H_4,2C_2H_5OH$, m.p. −31·2° was formed.[42] In the hydrazine nitrate–water system no hydrates were detected[43]; similarly no compound formation was suggested by results of investigation of the hydrazine nitrate–alkali metal nitrate and hydrazine–urea systems.[44, 45] Confirmation of existence of a complex, N_2H_4,AcOH, indicated by earlier thermal analysis of a number of hydrazine–organic acid systems,[43] was obtained by viscosity and specific gravity measurements in the system hydrazine–acetic acid.[46]

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SPECTRA OF HYDRAZINE

A wide range of spectroscopic techniques has been applied to the examination of hydrazine. In the Schumann region (vacuum ultra-violet), the moment of inertia of hydrazine has been determined,[1] and the heat of dissociation is given as 122·4 g.-cal. per mole. In the quartz ultra-violet region, hydrazine vapour exhibits[2] five bands with heads at approximately 2326, 2300, 2276, 2250, and 2225 A.; the bands are degraded towards shorter wave-lengths and fade into a region of general absorption, starting at 2200 A. The end-absorption of aqueous hydrazine becomes noticeable[3] between 248 and 230 mμ.

In the near infra-red region, around 1μ, hydrazine shows a wide diffuse band similar[4] to that found in ammonia and other amines and amides; this band may be[5] the third harmonic of the NH band. This band does not appear[6] in hydrazine dihydrochloride, as no trivalent nitrogen atom is present, but is found in the spectrum of the monohydrochloride. More detailed analyses[7, 8] have resolved this band further into one principal and two less intense subsidiary bands which occur[7] for liquid hydrazine (and hydrate, respectively) at 1·07 to 1·06 μ (1·06–1·05 μ), 1·034 μ (1·026 μ) and 1·0225 μ (1·012 μ).

Over the infra-red region between 1·5 and 25 μ, hydrazine vapour exhibits some twenty bands, assignment of which is, however, difficult because of the extensive overlapping.[9] The spectrum shows[10, 11] some changes with temperature which may be correlated with rotational changes of the molecule. In the crystal at −190°, hydrazine is in the unsymmetrical *trans*-configuration[10] and liquid and gaseous materials exist as equilibrium mixtures of the three conformational forms. The heat of vaporization is about 10 kcal. per mole and the molecule is associated.[11] Some of the infra-red bands reported correspond to the Raman lines; the others are assumed[12] to be combination frequencies.

The infra-red spectra of hydrazine hydrochloride and hydrobromide have also been studied[13] in some detail.

In the micro-wave region between 4·7 and 30×10^9 sec.$^{-1}$ about 200 lines with quadratic Stark effects were found[14] in the hydrazine spectrum.

The Raman spectrum of hydrazine was recorded by several workers[15, 16, 17, 18, 19, 20] in the period 1930–1940. Essentially it consists of three[14] or five[15] lines; again, as in the infra-red spectrum,[5] some of the lines do not occur[16] in the Raman spectrum of the dihydrochloride.

More recently, nuclear magnetic resonance spectra have been reported for hydrazine[21] and for hydrazine dihydrofluoride,[22] $N_2H_4,2HF$. The chemical shift of the ^{14}N resonance relative to the nitrite ion normalized to 10,000 gauss was[21] 5·66 gauss. In the dihydrofluoride, the N—H bond length calculated[22] was 1·075 ± 0·02 A. and the F to H distance 1·542 ± 0·01 A.; the derived N—F distance of 2·62 A. agrees well with that determined by *X*-ray crystallography. The very strong hydrogen-bonding properties in this salt were obvious from the spectrum.

The proton-magnetic resonance spectra of hydrazine salts have also been reported[23]; the sulphate N_2H_4,H_2SO_4 undergoes a transition near 150°K. interpreted as a rotational change of the $N_2H_6^{2+}$ ion about the N–N axis, with a potential barrier of 3 to 4 kcal. per mole.

The free radical absorption spectrum of hydrazine produced by a flash discharge has also been reported.[24] The presence of these radicals and other decomposition products can be detected[25] mass-spectrometrically. The mechanism by which the free radicals arise is discussed on pages 83, 97.

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THE CHEMICAL PROPERTIES OF HYDRAZINE

Much of the fundamental inorganic chemistry of hydrazine was investigated during the thirty years or so after it was first isolated in 1887 by Curtius and has been reported in Mellor (VIII, 312–320). Considerable extension of this knowledge during the last forty years is concerned particularly with the constitution of hydrazine and its salts and complexes and with its reactions with organic compounds.

Hydrazine can be regarded as a member of one of the saturated series of hydronitrogens of formula N_nH_{n+2} comprising ammonia NH_3, hydrazine or diamide N_2H_4, triazane N_3H_5, and tetrazane N_4H_6, etc. There are also three unsaturated series of formulae N_nH_n, N_nH_{n-2}, and N_nH_{n-4}.

Table II.—Hydronitrogens

Saturated Hydronitrogens	Unsaturated Hydronitrogens		
N_nH_{n+2}	N_nH_n	N_nH_{n-2}	N_nH_{n-4}
NH_3 (ammonia)			
N_2H_4 (hydrazine)	N_2H_2 (di-imide)		
N_3H_5 (triazane)	N_3H_3 (triazene)	N_3H (hydrazoic acid)	
N_4H_6 (tetrazane)	N_4H_4 (tetrazene)		
	N_5H_5 (hydrazine azide)	N_5H_3 (bisdiazoamine)	
		N_6H_4 (hexazodiazene)	
		N_7H_5 (heptazodiazene)	
			N_8H_4 (octazone)

Many of these hydronitrogens are known only as organic derivatives. Obviously the saturated series is the most stable; the N–N bond is however readily broken and in each homologous series the stability of the compounds decreases as the series is ascended.[1,2] Interconversion between one series and another is possible in spite of the instability of almost all of these compounds; e.g., unsaturated hydrazoic acid has been successfully reduced to hydrazine.[3]

Hydrazine can also be regarded as a member of a nitrogen series derived from ammonia, analogous to a series derived from water and to another series derived from water and ammonia[4]; in these last series it corresponds to hydrogen peroxide and hydroxylamine, which have similar solvent properties and undergo parallel chemical reactions. It is found that in each case the member of the ammonia series is more strongly basic and more strongly reducing than the corresponding member of the water series, whilst members of the mixed series occupy an intermediate position.[5] The position of hydrazine in these two series forms a useful background against which to consider its basic decomposition, its oxidation and reduction reactions and its reactions with nitrogen, all of which have now been studied in some detail.

Decomposition of Hydrazine

The decomposition of anhydrous hydrazine has been examined under a wide range of conditions and with many different means of excitation.

The homogeneous reaction has been studied using photochemical,[6,7,8,9] thermal,[10,11,12,13,35] electrical (sparking,[14] high frequency oscillation,[15] and glow discharge[16,17,18,19]), and electromagnetic[20,21] methods of initiating the decomposition, principally at low pressures. These results suggest a first-order reaction although the activation energy (25–36 kcal.) is much lower than that required for the unimolecular reaction $N_2H_4 \rightarrow 2NH_2$ (60 kcal.). Flame speed studies,[22,23,24,25] however, suggest that the rate-determining process is of the second order, and a chain mechanism in which NH_2 is formed by a pseudo-unimolecular process tending to first order at high pressures but to second order at low pressures seems likely. The effect of inert gases such as hydrogen, nitrogen, argon, and toluene on the thermal decomposition is explained in terms of the thermal capacities of these gases. Studies of the explosive decomposition indicate that hydrazine does not detonate.[26,27]

The heterogeneous thermal decomposition of hydrazine[6,11,12,28] follows one of two reactions: $3N_2H_4 \rightarrow N_2 + 4NH_3$ on quartz,
or $2N_2H_4 \rightarrow H_2 + N_2 + 2NH_3$, e.g., on platinum or tungsten wire.[10]
The catalytic decomposition of hydrazine on Raney nickel occurs at room temperature and has a very low activation energy (17·1 kcal/mol.). The rate of decomposition increases with the addition of water to a maximum in 6 to 10 M. hydrazine solutions,[29,30] and it is suggested that water even in very small amounts may play a part in the reaction, as it appears to do in the non-catalytic decomposition of hydrazine hydrate.[31,32,33,34]

OXIDATIVE DECOMPOSITION

In further attempts to elucidate the mechanism of decomposition of hydrazine its thermal[14,23,25,36–41] and photochemical[42,43] decomposition in presence of oxygen and other oxidizing agents such as nitric oxide, hydrogen peroxide, or hydroxylamine, both in the gas phase and in aqueous solution,[44–47] has been studied. The rate-determining process appears to be of the second order. Small amounts of copper and iron act as catalysts[46,47,48,49,50,51] and greatly increase the reaction rates, particularly in the case of auto-oxidation; it is suggested that this may be due to the formation of active oxygen at the catalyst surface.

It is interesting that hydrazine reacts also with atomic hydrogen[52,53,54,55] to give ammonia, possibly through an intermediate N_2H_3,[56] and with atomic nitrogen to give nitrogen, hydrogen, and ammonia.[57]

OXIDATION OF HYDRAZINE IN SOLUTION

Since hydrazine undergoes auto-oxidation in aqueous solution,[46, 47, 48, 49] it will obviously react with oxidizing agents. While most oxidation reactions yield a mixture of ammonia and nitrogen, some first give hydrazoic acid, and a few give nitrogen only. Oxidation occurs in several steps and several free radicals have been detected as intermediates.[58, 59, 60, 61] The mechanism of oxidation has been shown to depend on the nature of the oxidants. One-electron transfer agents, such as ferric and cupric salts and monatomic halogens, convert hydrazine into ammonia and nitrogen with the hydrazoyl radical N_2H_3 as the primary intermediate.[59, 62] Two-electron transfer agents, such as chlorates, iodate, and hydrogen peroxide, produce hydrazoic acid as well as ammonia and nitrogen, with di-imide N_2H_2 as the primary intermediate. More complex oxidants such as potassium permanganate and ammonium metavanadate are reported to behave as mixtures of one- and two-electron transfer agents, although permanganate has also been classified as a simple two-electron transfer agent.[65] These general mechanisms and products are modified by the reaction conditions and specially by the presence of catalysts such as ferric or cupric ions; hydrazoic acid is formed in hot strongly acidic solutions by the action of two-electron transfer agents on hydrazine, but in cold, dilute acid solutions nitrogen (sometimes with a trace of ammonia) is formed.[58]

Kinetic studies of the oxidation of hydrazine include reactions with nitrogen dioxide yielding nitric oxide and nitrogen,[66] with ferricyanide[67, 68] where the reaction rate can be increased by irradiation,[69] with permanganate,[60, 70, 71, 72] with ceric sulphate,[73] with iodine,[74] and with hypobromite and hypochlorite.[75] The catalytic action of iron,[57] silver,[76] osmium tetroxide,[77] rhenium,[78] and platinum and palladium[79] has also been studied.

Salts of Hydrazine

SIMPLE SALTS

Hydrazine is dibasic and can form two series of salts, N_2H_4,HA and $N_2H_4,2HA$; the diacid salts dissociate into the mono salt and the free acid when dissolved in water.[80] The nomenclature of hydrazine salts is based on usage rather than on scientific accuracy; for example, there are three hydrazine sulphates, usually known as monohydrazine sulphate, N_2H_4,H_2SO_4, dihydrazine sulphate, $(N_2H_4)_2,H_2SO_4$, and hydrazine disulphate, $N_2H_4,(H_2SO_4)_2$. The mono salt is often referred to simply as hydrazine sulphate, but systematically it should be called hydrazonium (or hydrazinium) hydrogen sulphate since it contains the $N_2H_5^+$ ion analogous to the NH_4^+ ammonium ion. Alternatively the N_2H_5 ion can be regarded as a hydrazinium ion[81] so that $N_2H_5HSO_4$ and $(N_2H_5)_2SO_4$ can be named hydrazinium hydrosulphate and hydrazinium or dihydrazinium sulphate, respectively. To make the situation more confusing these three sulphates used to be described as hydrazine disulphate, hydrazine monosulphate and hydrazine hydrodisulphate respectively (Mellor, VIII, 325–6). Similarly, N_2H_4,HCl or N_2H_5Cl is referred to as hydrazine monohydrochloride (not hydrazonium chloride) and $N_2H_4,2HCl$ as hydrazine dihydrochloride.

In spite of these anomalies in their nomenclature, these simple salts are well known and have been fully described (Mellor, VIII, 325–6). Very few new salts have been recently prepared but the physical and chemical properties of these salts have been extensively studied during the last thirty years.

The crystal structure of hydrazine dihydrofluoride has been examined,[82, 83] and its interatomic distances have been determined by nuclear magnetic resonance[84] technique; similar studies of hydrazine dihydrochloride[85, 86, 87] and hydrazine monohydrobromide[88] have been reported. Physical properties such as heat capacities, heats of solution,[89, 90] dissociation pressures and temperatures,[91–93], conductance, viscosity,[94] pH,[95] and diamagnetism[96] of a number of hydrazine mono- and dihydro-halides have been investigated. A description of a two-stage industrial process for the preparation of hydrazine monohydrobromide by the reaction of ammonium bromide, prepared from ammonia and bromine, with hydrazine has been published,[97] and new dihydrates of hydrazine dihydrobromide and iodide $N_2H_4,2HBr,2H_2O$ and $N_2H_4,2HI,2H_2O$ have been described.[92, 93] The interconversion of halides, in particular the chlorides and iodides, has been studied.[98]

Table III.—Crystal Structure of Simple Hydrazine Salts

Compound	Crystal Form	Lattice Parameters	Interatomic Distances
$N_2H_4,2HF$	Rhombohedral	$a = 5{\cdot}43$ A.	N–N = 1·42 A.
		$\alpha = 38° 10'$	N–H = 1·05 A.
			N–H–F = 2·62 A.
$N_2H_4,2HCl$	Cubic	$a = 7{\cdot}89$ A.	N–N = 1·42 A.
N_2H_4,HCl	Orthorhombic	$a = 12{\cdot}49$ A.	N–N = 1·45 A.
		$b = 21{\cdot}85$ A.	N–H–N = 2·95 A.
		$c = 4{\cdot}41$ A.	$\overset{+}{N}$...Cl ~ 3·12 A.
			N...Cl ~ 3·4 A.
N_2H_4,HBr	Monoclinic	$a = 12{\cdot}85$ A.	N–N = 1·45 A.
		$b = 4{\cdot}54$ A.	
		$c = 11{\cdot}94$ A.	
		$\beta = 110° 16'$	
N_2H_4,H_2SO_4	Orthorhombic	$a = 8{\cdot}251$ A.	N–N = 1·40 A.
		$b = 9{\cdot}159$ A.	N–H...O = 2·73 and 2·77 A.
		$c = 5{\cdot}532$ A.	
			N–H = 2·79–2·99 A.
			S–O = 1·48–1·49 A.
N_2H_4,HNO_3	Monoclinic	$a = 11{\cdot}23$ A.	
		$b = 11{\cdot}73$ A.	
		$c = 5{\cdot}17$ A.	
		$\beta \sim 90°$	

The highly explosive hydrazine perchlorate has been prepared by mixing 75% aqueous hydrazine hydrate with 60% aqueous perchloric acid at 0°C.; the salt melts at 137–138°, has $d_{15}^{15} = 1{\cdot}939$ and decomposes between 145° and 230°; it is fairly soluble in water but insoluble in organic solvents[99]; the conductivity at 25° is 125·2 mhos.[100] The corresponding chlorite, $N_2H_4,HClO_2$, which is also explosive, has been prepared by treating the sulphate, N_2H_4,H_2SO_4, with 0·5 equivalent of barium hydroxide and 0·5 equivalent of barium chlorite at 0–2°. Hydrazine chlorite separates when the filtered solution is poured into ethanol at −10°; it is highly inflammable when dry.[101]

Physical studies of hydrazine sulphates are fewer than of the halides but the crystal structure of the orthorhombic hydrazine monohydrosulphate N_2H_4,H_2SO_4[102] (see Table III), its solubility,[103] equilibrium relative humidity (saturated solution),[104] and change in density with temperature (10% solution),[105] have also been reported. Hydrazine sulphate is sparingly soluble in cold water (Mellor, VIII, 325); its solubility[103] in water at 94° is 14%, at 152° 40% and at 198° 60%. Decomposition begins to set in above 200°. An interesting capillary electric effect has been described: in concentrated solutions made alkaline by addition of hydrazine hydrate rapid solution transfer occurs from the anodic to the cathodic compartment of a two-compartment cell under conditions below the decomposition potential of hydrazine monohydrosulphate.[106]

The corresponding hydroselenate N_2H_4,H_2SeO_4 is prepared by the action of hydrazine hydrate on dilute aqueous selenic acid. It is explosive, sparingly soluble in cold but readily soluble in hot water, and decomposed by hydrochloric acid to give selenium.[107]

Hydrazine polysulphide, $(N_2H_5)_2S_n$, is prepared by the action of hydrogen sulphide on hydrazine hydrate; it yields water-soluble hydrazine tetrathionate, $(N_2H_5)_2S_4O_6$, with a decomposition temperature of 85–87°, on prolonged reaction with oleic acid.[108]

Hydrazine nitrate, N_2H_4,HNO_3, m.p. 70·5°, is prepared by the action of the equivalent amount of barium nitrate on hydrazine monohydrosulphate in vacuo at −5°.[109] Its crystal structure has been studied[110] (see Table III), and the density, viscosity, and electrical conductance of concentrated aqueous solutions of the salt have been measured.[94] At 0·23, 0·98, 4·25, 15·8 and 38·7 mol.-% the density of the solutions at 25° is 1·002, 1·018, 1·083, 1·242 and 1·403 g. per ml., respectively, and the viscosity 0·895, 0·892, 0·951, 1·580 and 4.437 centipoises, respectively. The salt is less stable than ammonium nitrate and its explosive properties have been studied in some detail.[111]

Hydrazine azide, N_2H_4,N_3H, can be prepared by the action of hydrazine on ammonium azide under almost anhydrous conditions[112]; it is explosive[113] and has m.p. 75·4°.[114] It reacts with hydrazine to give a solvate, N_2H_4,N_3H,N_2H_4, m.p. 66·4°,[114] similarly with ammonia to give $2(N_2H_4,N_3H),NH_3$ which is a deliquescent colourless crystalline solid; in liquid ammonia it undergoes ammonolysis to hydrazine and ammonium azide above −9°, and gives the compound $NH_4N_3,2NH_3$ below −9°.[115]

The kinetics of the transformation of hydrazine cyanate, $N_2H_4,HCNO$, into semicarbazide, which proceeds readily at room temperature, have been studied,[116] and the heat of combustion of hydrazine thiocyanate $N_2H_4,HCNS$ has been measured[117]; a study of the isomerization of hydrazine selenocyanate, $N_2H_4,HCNSe$, is reported. The compound is stable in aqueous solution at 95° for 213 hours but isomerizes rapidly to give 35% selenosemicarbazone in presence of acetone.[118]

COMPLEX SALTS AND COMPLEXES OF HYDRAZINE

Hydrazine forms a large number of double or more complex salts such as halogenoberyllates, -borates, -aluminates, -stannates etc., and also gives rise to complexes (similar to those formed by ammonia) and chelated compounds in which hydrazine acts as a bidentate chelating agent; this bridging effect may lead to the formation of polycationic complexes and explains the insolubility of many hydrazine complexes. There is also some tendency to the formation of a weakly bound intermolecular complex.

Two fluoroberyllates have been described in the literature: hydrazinium fluoroberyllate, $N_2H_4,BeF_2,2HF$, prepared by the action of hydrazine hydrochloride on silver fluoroberyllate, Ag_2BeF_4,[119] and hydrazine hydroxyfluoroberyllate $N_2H_4,BeFOH,2HF$ prepared by the trituration of hydrazine hydrochloride with a solution of thallium hydroxyfluoroberyllate Tl_2BeF_3OH.[120] Both are water-soluble double salts.

Anhydrous hydrazine reacts with excess of diborane, B_2H_6, at 0° to give a white hygroscopic solid of approximate composition $BN_{1.2}H_{4.8}$, thought to be a complex salt[121]; in ether at −80° a white crystalline solid of formula N_2H_4,B_2H_6 is formed.[122] Hydrazine fluoroborate N_2H_4,BF_3,HF is prepared by the action of 30% HBF_4 on hydrazine hydrate and evaporation to crystallization,[123] or by heating hydrazine with boron trifluoride etherate, BF_3,Et_2O, at 60–100°[124]; it is nonhygroscopic and readily soluble in water. An intermolecular complex, having structure similar to that of graphite, between boron nitride and hydrazine, has been reported.[125]

Hydrazine fluoroaluminate, $N_2H_4,AlF_3,2HF$, prepared by the action of hydrazine dihydrofluoride on aluminium fluoride[126]; and hydrazinium hexachloro- and hexabromo-aluminates, $3N_2H_4,AlCl_3,3HCl,6H_2O$, and $3N_2H_4,AlBr_3,3HBr$, d_{17}^{17} 1·55 and 2·25 respectively, form deliquescent solids, dissolving in their own water of crystallization at 142 and 150° respectively but giving clear melts at 194–196° and at 192° respectively; they are prepared by crystallization over sulphuric acid and sodium hydroxide of mixtures of the corresponding aluminium halide and hydrazine hydrohalide.[127] Hydrazonium alum, $N_2H_4,HAl(SO_4)_2,12H_2O$, is prepared by crystallization of an aqueous solution of hydrazine sulphate and aluminium sulphate.[128] Double halides of indium and hydrazine of general formula $InX_3(N_2H_4)_3$, where X is halide, are prepared by the direct reaction of anhydrous hydrazine with the corresponding indium halide.[129]

Members of two series of hydrazine tin halide double salts have been reported corresponding to the di- and tetra-valent states of tin. Dihydrazinium hexafluorostannate, $2N_2H_4,SnF_4,2HF$, m.p. 194–196° (with decomposition), is prepared by the action of hydrazine hydrate acidified with hydrofluoric acid on freshly prepared stannous fluoride and evaporation to crystallization.[130] The corresponding chloride, $2N_2H_4,SnCl_4,2HCl$, which forms orthorhombic crystals ($a = 11{\cdot}8$ A., $b = 11{\cdot}8$ A., $c = 8{\cdot}2$ A.)[131] is prepared from stannous chloride and hydrazine dihydrochloride, $N_2H_4,2HCl$,[132] and the dihydrazinium hexabromostannate, $2N_2H_4,SnBr_4,2HBr$, a yellow deliquescent salt, is prepared by adding first tin foil to excess of well cooled bromine, then 48% hydrobromic acid and a little water, followed (after removal of excess of bromine) by 28% hydrazine hydrate and crystallization over sodium hydroxide.[127] Hydrazinium hydrogen tetrafluorostannite, $N_2H_4,SnF_2,2HF$, is prepared by the rapid evaporation to crystallization of a solution of freshly prepared stannous hydroxide in hydrazine hydrate acidified with hydrofluoric acid.[130] There is no record of the corresponding chloride, but two bromides have been reported: hydrazinium tribromostannite, $N_2H_4,SnBr_2,HBr$, which forms orthorhombic crystals decomposing at 150–180°, is prepared by crystallization from a solution of stannous bromide and hydrazine hydrobromide in warm water or 50% aqueous ethanol,[127] and dihydrazinium tetrabromostannite, $2N_2H_4,SnBr_2,2HBr,H_2O$, a deliquescent solid, m.p. 81–83°, readily oxidized in air, which is also prepared by causing stannous bromide to react with hydrazine hydrobromide in warm water but which separates on addition of a three-fold excess of ethanol.[127]

Although there is evidence for the existence of a hydrazine fluoroarsenate it has not been isolated, but hydrazinium hexafluoroantimonate, N_2H_4,SbF_5,HF,H_2O, which is prepared by the action of hydrazine hydrate on a solution of antimony pentoxide in aqueous hydrofluoric acid,[130] and a large number of halo-antimonites and -bismuthites, which are prepared by the action of the hydrazine hydrohalides on the freshly prepared antimony or bismuth trihalide in acid solution, have been reported.[130, 133] In all cases these salts are very soluble in water, decomposing on dilution to give the insoluble basic antimony or bismuth halides; the chlorides are colourless, the bromides yellow, and the iodides red.

Table IV.—Hydrazinium Haloantimonites and Halobismuthites[133]

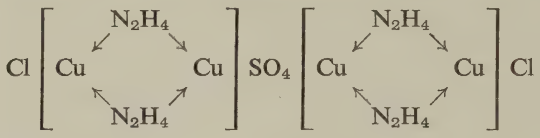
$N_2H_4,SbF_3,2HF$	$N_2H_4,BiF_3,2HF$
$2N_2H_4,SbCl_3,2HCl$	$2N_2H_4,BiCl_3,2HCl$
	$N_2H_4,BiCl_3,HCl$
	$N_2H_4,BiCl_3,2HCl,2H_2O$
	$4N_2H_4,BiBr_3,4HBr$
	$3N_2H_4,BiBr_3,3HBr$
	$N_2H_4,BiBr_3,2HBr,4H_2O$
$11N_2H_4,2SbBr_3,11HBr$	
$3N_2H_4,2SbBr_3,3HBr$	$3N_2H_4,2BiBr_3,3HBr$
$10N_2H_4,3SbBr_3,10HBr$	
	$6N_2H_4,3BiBr_3,7HBr,10H_2O$
$3N_2H_4,SbI_3,3HI$	$3N_2H_4,BiI_3,3HI$
$N_2H_4,SbI_3,HI,3H_2O$	
	$5N_2H_4,3BiI_3,5HI,6H_2O$
	$6N_2H_4,4BiI_3,7HI,10H_2O$

In addition to the formation of hydrazine hydrosulphide previously reported (Mellor, VIII, 314), the zinc and cadmium complex selenides $N_2H_4,ZnSe$ and $N_2H_4,CdSe$ have been prepared by action of 85% hydrazine hydrate on the metallic selenites; the copper, mercury and lead selenites are reduced to selenides, and alkali metal selenites are reduced by dilute aqueous hydrazine to a mixture of the selenide and selenium.[134]

Work on hydrazine sulphonic acid has also been greatly extended and, in addition to hydrazine monosulphonic acid, the di-, tri-, and tetra- sulphonic acids have now also been isolated, together with a number of their metallic salts,[135] as also has hydrazine sulphonamide.[136]

It is interesting that although hydrazine appears to form only co-ordination complexes with copper salts its compounds with silver are of a salt-like character.

Reaction of hydrazine with the corresponding silver salt under anhydrous conditions and in organic solvents such as diethyl ether, pyridine, ethanol and methanol yields the hydrazinates of silver thiocyanate, $N_2H_4,AgCNS$, of silver cyanide, $N_2H_4,AgCN$, of silver nitrate, $N_2H_4,AgNO_3$, of silver sulphate, $3N_2H_4,Ag_2SO_4$, of silver chloride, $N_2H_4,3AgCl$, of silver bromide, $N_2H_4,3AgBr$, and of silver iodide, $N_2H_4,2AgI$; these compounds all decompose in presence of water to give metallic silver and nitrogen.[137] With copper a dark brown crystalline complex $4N_2H_4,Cu_2SO_4,2CuCl$[138] is formed by dropwise addition of N. cupric solution to hydrazine sulphate in 5% potassium hydroxide solution. This complex probably has the constitution:



$$\mathrm{Cl}\left[\begin{array}{ccc} & N_2H_4 & \\ \swarrow & & \searrow \\ \mathrm{Cu} & & \mathrm{Cu} \\ \nwarrow & & \nearrow \\ & N_2H_4 & \end{array}\right]\mathrm{SO_4}\left[\begin{array}{ccc} & N_2H_4 & \\ \swarrow & & \searrow \\ \mathrm{Cu} & & \mathrm{Cu} \\ \nwarrow & & \nearrow \\ & N_2H_4 & \end{array}\right]\mathrm{Cl}$$

The hydrazinate of copper chlorate has also been prepared by the addition of hydrazine hydrate in aqueous ethanol to copper chlorate solution; the complex however is extremely explosive and detonates on drying at room temperature.[139]

A complex of calcium trinitride and hydrazine, $2N_2H_4,Ca(N_3)_2$, has been prepared by dissolution of the trinitride in anhydrous hydrazine and gradual evaporation of the excess of hydrazine; it is thought to be isomeric or possibly identical with the calcium derivative of either 1-pentazene or 2-pentazene.[140] The formation of complexes between Ca^{2+} and hydrazine is supported by potentiometric measurements of aqueous calcium nitrate–hydrazine mixtures.[141]

A polarographic study of hydrazine zinc complexes in perchlorate solution suggests that these are similar to the copper complex cited above and at $pH < 9$ zinc and hydrazine alone co-ordinate to give ions of the type $ZnN_2H_4^{++}$, $Zn(N_2H_4)_2^{++}$, $Zn(N_2H_4)_3^{++}$, and $Zn(N_2H_4)_4^{++}$; while at $pH > 9$ ions of the type $[Zn(N_2H_4)_3OH]^+$ or $[Zn(N_2H_4)_2(H_2O)OH]^+$ exist in solution.[142] Complex nitrates of zinc and cadmium with hydrazine of the formulae $3N_2H_4,Zn(NO_3)_2$ and $3N_2H_4,Cd(NO_3)_2$ have been prepared by addition of a 20–30% solution of the metal nitrate in water or ethanol to hydrazine in 40% aqueous ethanol at 10–20°; both are moderately stable white crystalline powders burning at 310° and 236–245°, respectively.[143] The highly explosive $3N_2H_4,Cd(ClO_4)_2,Cd(OH)_2,H_2O$ has been similarly prepared.[139] Zinc bisulphite treated with sulphur dioxide in aqueous hydrazine solution yields $2N_2H_4,ZnSO_3,1{\cdot}5H_2O$, a white sparingly soluble complex which with excess of sulphur dioxide gives $N_2H_4,ZnSO_3,H_2SO_3$. Cadmium sulphite similarly forms $N_2H_4,CdSO_3$ and $N_2H_4,CdSO_3,H_2SO_3$. Hydrazine also reacts with cadmium nitrite to give the white explosive complex $2N_2H_4,Cd(NO_2)_2$,[144] and with zinc and cadmium thiocyanate in the presence of ammonium thiocyanate to give the sparingly soluble complexes $2N_2H_4,Cd(SCN)_2$ and $2N_2H_4,Zn(SCN)_2$ which are hydrolysed in hot water to the metal hydroxides.[145] Complex mercury halides appear to have a similar constitution and several have been isolated. $(N_2H_4Hg_2)Cl_2$, which is highly explosive,[146] is obtained in rhombic crystals ($a = 8{\cdot}15$, $b = 6{\cdot}75$, and $c = 10{\cdot}55$ A.) by precipitation with solid sodium acetate from an ice-cold aqueous solution of hydrazine hydrochloride and mercuric chloride[147]; the compounds $2N_2H_4,HgCl_2$, $N_2H_4,HgCl_2$ and $N_2H_4,HgBr_2$ have also been isolated.[148]

Three hydrazine complexes of manganese have been reported based on the formation of $Mn(N_2H_4)_2^{++}$: the sparingly soluble thiocyanate $2N_2H_4,Mn(CNS)_2$ prepared by addition of hydrazine sulphate to manganese thiocyanate in ammoniacal solution containing excess of ammonium thiocyanate[145]; the sparingly soluble acid sulphite $N_2H_4,MnSO_3,H_2SO_3$ (prepared by the action of hydrazine on manganese sulphite in presence of excess of sulphurous acid) which is hydrolysed by ammonia, precipitating manganese hydroxide[144]; and the relatively stable yellow nitrate, $2N_2H_4,Mn(NO_3)_2$, which ignites at 150° and is prepared by addition of aqueous or ethanolic nitrate to 40% ethanolic hydrazine at 10–20°.[143] In addition the mixed tungsten or molybdenum complex cyanides of formulae $Mn_2[W(CN)_8(N_2H_4)_2],4H_2O$ and $Mn_2[Mo(CN)_8(N_2H_4)_2],4H_2O$ have been prepared. They are of interest not only because of their stability (they are red, water-insoluble compounds), but also because they are examples of complexes in which tungsten and molybdenum have co-ordination numbers of ten.[149]

Several complex iodides of chromium have been isolated as a result of an anhydrous reaction between hydrazine and chromium iodide (in benzene solution). These include $6N_2H_4,CrI_2$ and $4N_2H_4,CrI_2$ which are obtained by direct evaporation of the benzene solution over sulphuric acid; treatment of the benzene solution with ethanol yields $5N_2H_4,Cr_2(OEt)_2.I_2$ which on evaporation under high vacuum gives[150] $3N_2H_4,CrI_2$ which in turn on treatment with water gives $5N_2H_4,Cr_4(OH)_4.I_4,6H_2O$. There is some evidence for the existence of the corresponding chloro-complexes but none has so far been isolated.[158] There is also some evidence (*X*-ray and thermal desorption studies) for the existence of two uranium hydrazine complexes, but neither has been isolated.[151]

Hydrazine ferrocyanide forms complexes with copper, zinc, iron, cobalt and nickel salts analogous to the complex ammonium ferrocyanides[152]; a complex carbonyl hydrazine compound is formed by the reaction of iron pentacarbonyl with hydrazine,[153] and a hydrazine complex with ferrous dimethylglyoxime has been examined physically and found to resemble the corresponding ferrous porphyrin.[154]

A large number of complexes of cobalt and nickel have been isolated and studied and are listed in Table V[139, 143–145, 155–160]; most of these complexes are of the types $[MN_2H_4]^{++}$ and $[M2N_2H_4]^{++}$. Their preparation is usually effected by the action of the corresponding hydrazine salt on the cobalt or nickel salt, sometimes under anhydrous conditions.

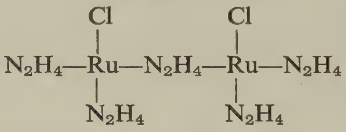
Table V.—Cobalt and Nickel Hydrazine Complexes

Halides	$2N_2H_4,CoCl_2$	$3N_2H_4,NiCl_2$
		$2N_2H_4,NiCl_2$
Halates		$3N_2H_4,Ni(ClO_3)_2$
		$5N_2H_4,2Ni(ClO_4)_2,NiClO_4OH,3H_2O$
Sulphates		$3N_2H_4,NiSO_4$
Sulphites		$3N_2H_4,NiSO_3,H_2O$
		$3N_2H_4,4NiSO_3,7H_2O$
	$2N_2H_4,CoSO_3,H_2O$	$2N_2H_4,NiSO_3,H_2O$
	$2N_2H_4,CoSO_3,H_2SO_3,2H_2O$	
	$N_2H_4,CoSO_3,H_2SO_3$	
	$N_2H_4,2CoSO_3,2H_2O$	
Nitrates	$3N_2H_4,Co(NO_3)_2$	$3N_2H_4,Ni(NO_3)_2$
		$2N_2H_4,Ni(NO_3)_2$
		$N_2H_4,Ni(NO_3)_2$
Nitrites	$3N_2H_4,2Co(NO_2)_2$	$2N_2H_4,Ni(NO_2)_2$
Carbonates	$2N_2H_4,Co(HCO_3)_2$	
	$N_2H_4,Co(N_2H_3CO_2)_2$	
	$[4N_2H_4,Co(CO_2)_2]CO_3$	
	$[N_2H_4,Co(NH_3)_4NO_2]CO_3$	

The structure of sodium hydrazine cobaltinitrite, $NaN_2H_6Co(NO_2)_6$, has been studied.[161] An abortive attempt has been made to prepare hydrazine nickel perchlorate, $2N_2H_4,Ni(ClO_4)_2$,[162] and hydrazine complexes of nickel bromide, pyrophosphate and cyanide have been prepared.[158, 160]

Among the platinum metals, complexes of platinum and palladium have been studied in some detail, while a number of complexes of ruthenium have also been reported. Simple complexes of platinum and palladium of the types $MN_2H_4^{++}$ and $M(N_2H_4)_2^{++}$ (see Table V)[163] appear to be formed by mixing hydrazine hydrochloride with the appropriate potassium platinum or palladium double salt.

Ruthenium forms more complex anions involving Ru—N_2H_4—Ru bridges[164] as in the $Ru_2(N_2H_4)_5Cl_2^{4+}$ anion for which the structure:



$$\begin{array}{ccccc} & Cl & & Cl & \\ & | & & | & \\ N_2H_4— & Ru & —N_2H_4— & Ru & —N_2H_4 \\ & | & & | & \\ & N_2H_4 & & N_2H_4 & \end{array}$$

is proposed and which has been isolated as the chloride, platinichloride, and bisulphate; similar structures are proposed for the complexes $[Ru_2(N_2H_5)_4,N_2H_4.Cl_6]Cl_4,HCl$ and $[Ru_2(N_2H_4)_5.Cl](HSO_4)_4,3H_2SO_4,3H_2O$. This bidentate bridge structure is shown also by some organic hydrazine platinum complexes[165] which form anions of the type:

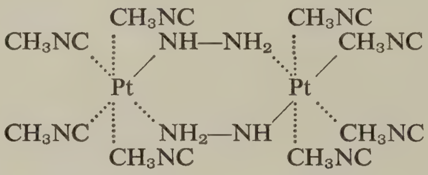


Table VI.—Hydrazine Complexes of Platinum and Palladium

$PtCl_2,(N_2H_4)_2$	$PdCl_2,(N_2H_4)_2$
	$PdCl_2,(N_2H_4)_2,H_2O$
$PtCl_2,N_2H_4$	$PdCl_2,N_2H_4$
$[PtCl_2,(N_2H_5)_2]Cl_2$	
$[PtCl_2,(N_2H_5)_2]SO_4$	
$[PtCl_2,(N_2H_5)_2](NO_3)_2$	
$[PtCl_2,(N_2H_5)_2]Cl_2,2H_2O$	$[PdCl_2,(N_2H_5)_2]Cl_2,2H_2O$
$[PtCl_2,N_2H_4,N_2H_5]Cl$	$[PdCl_2,N_2H_4,N_2H_5]Cl$
$PtBr_2,(N_2H_4)_2$	
	$PdBr_2,(N_2H_4)_2,H_2O$
$PtBr_2,N_2H_4$	$PdBr_2,N_2H_4$
	$[PdBr_2,(N_2H_5)_2]Br_2,4H_2O$
$2PtI_2,(N_2H_4)_2$	
$[Pt(N_2H_5.HSO_4)_4]Cl$	

Reactions of Hydrazine in Preparative Inorganic Chemistry

The properties of hydrazine which have proved of interest in preparative inorganic chemistry are its action as a reducing agent, its catalytic action, and its solvent properties.

REDUCTION REACTIONS

Iodoform may be prepared by the reduction of carbon tetraiodide with hydrazine in liquid ammonia.[166] Selenides can be prepared by reduction of selenites with hydrazine in acid solution but in alkaline solution the reaction is not quantitative.[167] Hydrazine hydrochloride reacts with cuprous oxide to give metallic copper, cuprous chloride, and nitrogen[168] and with arsenates to give arsenites or in 1·5 N. hydrochloric acid to give free arsenic and some arsine, AsH_3; a mechanism for the formation of the arsine is proposed.[169] Hydrazine does not reduce nickel salts in water or ammoniacal solutions except in the presence of palladium or platinum catalysts when reduction to the metal is almost quantitative.[170] Hydrazine hydrosulphate is used for the preparation of molybdenum blue in the cerulein molybdometric determination of phosphate, since it acts on only one of the two forms of phosphomolybdic acid to give a phosphorated molybdenum blue with a definite and constant light absorption curve; this action eliminates the empiricism of the method.[171] Hydrazine can also be used to reduce Mo(VI) only to Mo(V),[172] and to reduce chloroplatinates to chloroplatinites.[173] In a less direct way reduction with hydrazine may affect subsequent reactions; for example, pretreatment of lead oxalate with hydrazine substantially increases the rate of its thermal decomposition, probably owing to the formation of particles of metallic lead which catalyse the decomposition.[174]

CATALYTIC REACTIONS

Hydrazine accelerates the decomposition velocity of potassium persulphate at room temperature[175]; and the yield of borazoles is increased by substituting hydrazine hydrohalide for the corresponding ammonium salt in the reaction with boron trihalides.[176]

REACTIONS IN LIQUID HYDRAZINE

Hydrazine behaves similarly to ammonia in its properties as a solvent.[177] Its dielectric constant is higher than that of ammonia and so the equivalent conductance of salts dissolved in hydrazine is greater,[178] approaching the values in water. Hydrazine salts act as acids, and metallic hydrazides act as bases in anhydrous hydrazine, neutralizing each other to form a salt and hydrazine according to the equation:

$$NaN_2H_3 + N_2H_4,HCl \rightarrow NaCl + 2N_2H_4$$

Several synthetic reactions in liquid hydrazine have been reported, and are summarized in the treatment of complex salts and complexes of hydrazine.[129, 137, 140, 150, 151] In addition, silanes may be prepared by the reaction of magnesium silicide with hydrazine hydrochloride in anhydrous hydrazine.[179]

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USES AND APPLICATIONS OF HYDRAZINE

Hydrazine is a strong reducing agent, endothermic and difunctional; it is also closely related to ammonia, an important constituent of many biologically active amines in which substitution of the hydrazine for the amino group often leads to interesting changes in activity. These properties, either singly or in combination, have assured hydrazine (and its derivatives) widespread use ever since it became freely available on the large scale; several reviews of these uses have appeared,[1] some in more extensive reviews dealing with hydrazine and its properties.

REDUCING PROPERTIES

Hydrazine is a versatile reducing agent which is attractive in use because of its high content of available hydrogen and because it is oxidized to nitrogen and thus does not introduce impurities into the reaction medium. Its reaction with oxygen ultimately gives nitrogen and water and has been widely applied[2] to prevent corrosion by dissolved oxygen, particularly in high-pressure boiler systems. Such systems are normally de-aerated and the residual oxygen concentration is very low—of the order of 0·01 p.p.m.; hydrazine, at a similar concentration, but present in excess, prevents access of the oxygen to the walls of the boiler tubes by heterogeneous reaction[3] with the oxygen at the metal surface. Several other systems in which hydrazine or its derivatives prevent corrosion have been described.[4]

One of the oldest uses of hydrazine is in the preparation of silver mirrors[5]; it has been used in the re-activation of poisoned silver catalysts[6] and reduces many other metallic salts to the metal[7] which may be obtained in a finely divided form particularly suitable for use as catalysts.

The absence of a residue after reduction is important in the formulation of simple soldering fluxes[8] based on hydrazine hydrochloride and hydrobromide which, as a flux on copper or copper alloys, leave no residue to corrode the joint. More complex formulations are stated[9] to be useful as soldering fluxes for aluminium.

Hydrazine has been used[10] in the preparation of ammoniacal cuprous chloride solutions, and the removal of free chlorine from hydrochloric acid or of nitrogen oxides from sulphuric acid is also readily possible.[11] Hydrazine prevents peroxidation of glycol ethers[12] and discoloration of arylamines and phenols[13] and stabilizes solutions of formaldehyde[14] and also certain polymeric systems[15] including polyformaldehyde and poly-*N*-vinylpyrrolidinone. The reducing properties have further been applied in the formulation of certain flotation agents[16] and in stabilizing and reclaiming lubricating oils.[17]

Hydrazine derivatives are widely used as components of photographic developers[18]; their various modes of action have received considerable attention.

The reducing properties are of direct interest in analytical chemistry[19] where hydrazine is increasingly used as a reagent, e.g., for the determination of iodine,[20] active chlorine,[21] and oxygenated halide anions.[22] Moreover hydrazine has been used as a reagent in electrometric titration,[23] as an ancillary reducing agent[24] and as an anode depolarizer[25] in inorganic analysis, and derivatives such as semicarbazide are used as reagents for the detection and identification of aldehydes and ketones in organic analysis.[26]

REDUCING PLUS ENDOTHERMIC PROPERTIES

One of the major uses of hydrazine, and potentially the largest, is as a component of rocket propellants.[27] With oxidants such as liquid oxygen, hydrogen peroxide, nitric acid and fluorine, it gives a high exhaust velocity and hence a high specific impulse at relatively low combustion temperatures.[28] Moreover while anhydrous hydrazine has a high density compared with hydrocarbon fuels, the products of oxidation have low density. Hydrazine can be stored and handled without excessive hazard,[29] yet it is rapidly ignited catalytically, ignition delay being estimated[30] at less than 3 millisec. The disadvantage of the high melting point of hydrazine (2°C.) is

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overcome[31] by admixture with other substances such as *NN*-dimethylhydrazine, guanidine nitrate, aniline, or hydrogen sulphide.

Combination of hydrazine with an oxidizing agent in the solid state produces explosive compositions. Thus hydrazine nitrate explodes more readily than does ammonium nitrate and may be suitable for military purposes.[32]

APPLICATION DEPENDING ON THE DIFUNCTIONAL NATURE OF HYDRAZINE

Hydrazine may be regarded as the simplest diamine. It reacts readily with dibasic acids, such as adipic and sebacic acid, giving polymers that can be drawn into fibres.[33] Much of this work has potential commercial utility and the relevant patent literature[34] indicates that the type of polymer formed varies with the relative proportions of hydrazine and acid: equimolar proportions afford polyhydrazides, but polyaminotriazoles are obtained[35] when two equivalents of hydrazine are used. Hydrazine has also been used[36] as a major component in other polymeric systems. In general its presence makes the polymer or fibre more hydrophilic and more readily dyed, but the stability against attack by acids is decreased.

The difunctional nature of hydrazine has been applied to the cross-linking of polymeric materials; especially is vulcanized rubber strengthened without any change in suppleness.[37] Unvulcanized rubber may be stiffened[38] by incorporation of hydrazine. In acrylonitrile–acrylate copolymers the low heat-resistance is remedied[39] by cross-linking effected by dipping in hydrazine hydrate, and the dyeing properties of acrylonitrile polymers are improved[40] analogously. On the other hand polyester fibres such as Terylene are rapidly degraded[42] by treatment with hydrazine. Hydrazine may be used[41] for stripping ‘reactive’ dyes based on cyanuric chloride from cotton and other cellulosic fibres: this hydrazinolysis of the cyanuric ‘ester’ link, in relatively mild conditions, hardly affects the material which can be re-dyed as if it were new.

Inclusion of hydrazine increases the rigidity of urea–formaldehyde–ammonia resins.[43]

Biological Applications

Hydrazine derivatives find wide use in chemotherapy and have some other interesting biological properties. The best-known use is probably that of *iso*nicotinoy hydrazide (Isoniazid) as a tuberculostatic agent,[44] both therapeutic and prophylactic. It is also effective in lepromatous leprosy.[45] Several other hydrazides behave similarly, and one of them, cyanoacetohydrazide[46] is, in addition, the first drug[47] to prove effective against lungworm in cattle. Other hydrazine derivatives effective[48] against *Mycobacteria* include thiosemicarbazones; and derivatives of isatin thiosemicarbazone are among the first proven[49] anti-viral chemotherapeutic agents, active against pox viruses. A series of derivatives of 5-nitrofurfuraldehyde[50] includes important antibacterial drugs (e.g. nitrofurazone) based on hydrazine derivatives; they are of use in both human and veterinary medicine, and particularly widely administered for the fowl disease coccidiosis.

Hydrazine sulphate and some other salts have some fungicidal activity.[51] Certain *iso*propylhydrazides and hydrazine analogues of the pressor amines affect the central nervous system, and are potent inhibitors of the enzyme monoamine oxidase; they are used as psychostimulants[52] and cause increase in the brain level of serotomin and noradrenaline. Other hydrazine derivatives such as hydrazinophthalozine (apresoline) are useful as hypotensive agents.[53]

Finally, maleic hydrazide has some unique properties, in that it reduces the growth-rate of plants[54]; it is therefore applied to grass and hedges which then need not be cut, to tobacco plants where sucker-formation is inhibited, and to potato plants of which the tubers then fail to sprout on subsequent storage.

MISCELLANEOUS USES

Hydrazine and its salts act as chemical blowing agents[55] to expand rubber and plastic mixes, but the blowing agents in common use[56] are organic derivatives of hydrazine, particularly[57] benzenesulphonhydrazide and its analogues or azo-compounds (see also page 107) such as azoformamide or azo-(2-cyano-2-propane) (azo-*iso*butyronitrile). Blowing agents when heated decompose with gas evolution (nitrogen from the hydrazine fragment of the molecule); in this decomposition free radicals are formed and these agents, particularly azo-(2-cyano-2-propane), may also act as polymerization initiators.

The formation of free radicals in the decomposition or oxidation of hydrazine is, in fact, utilized in a variety of ways, particularly in emulsion polymerization[58] of vinyl and vinylidene compounds. Polymerization may also be induced[59] by the catalytic decomposition of hydrazine on a metal surface such as palladium, but in this system certain monomers act as catalyst poisons.

The use of hydrazine as a reducing agent in organic reactions also depends on the generation of free radicals in presence of oxygen donors.

Hydrazine is a polar substance that has been used as a solvent for polarography,[60] electrochemical investigations[61] and spectrophotometry.[62]

Hydrazine also dissolves hairs and has been suggested for depilation of wet-salted cattle hide.[63]

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ANALYSIS OF HYDRAZINE

Detection and Identification

A number of organic compounds suitable for the detection and identification of hydrazine have been described. Reaction with salicylaldehyde[1, 2, 3] in acid solution gives a compound exhibiting ultra-violet fluorescence which permits the detection of 5×10^{-10} g. of hydrazine at a dilution of $1:10^8$; hydroxylamine (below a 10-fold excess), nitrite, nitrate, azides, ammonium ions, and strong reducing agents do not interfere. Aqueous hydrazine sulphate reacts with ethanolic picryl chloride[4] to give a pink-violet colour as a spot test on filter paper; this permits the detection of 5×10^{-9} g. of hydrazine at a dilution of 1:400,000 whilst hydroxylamine (below a 10-fold excess) gives a yellow-orange spot and does not interfere. p-Dimethylaminobenzaldazine,[5] the azine of 2-nitro-1,3-indandione,[6] and the compound formed with dimethylglyoxime[7] in acid solution and in presence of calcium chloride and potassium cyanate have also been used for the detection of hydrazine, which can be identified in the presence of other amines by the preparation of its dicumarol salt (m.p. 199–201°).[8]

Of the inorganic reactions available, the formation of molybdenum blue permits the detection of 12×10^{-6} g. of hydrazine in the presence of hydroxylamine, but is not specific since other reducing agents interfere.[9–11] Reaction of hydroxylamine or hydrazine with ammoniacal cupric ferrocyanide or ferricyanide[12] gives a white precipitate detectable on test papers impregnated with lead dioxide or thallium oxide at concentrations of 2×10^{-7} and 3×10^{-7}, respectively. Hydrazine has been detected in *iso*nicotinic acid hydrazide solutions by the separation of red fibrous selenium from selenium dioxide reagent[13] and macro-quantities of the compound may be detected in presence of hydroxylamine by the selective evolution of ammonia which is liberated from hydroxylamine by boiling with sodium carbonate, glucose, and ferrous sulphate, but from hydrazine only with sodium hydroxide.[14] Paper chromatography has also been used for the separation and semiquantitative determination of hydrazine; hydrazine, hydroxylamine, ammonium salts, phenylhydrazines, and phenylhydroxylamine may be separated using a developer composed of ether 50 parts, methanol 30 parts, water 15 parts, and concentrated hydrochloric acid 4 parts,[15] while g.-quantities of hydrazine and hydroxylamine are separated from acidic solvents and determined with picryl chloride.[16] (See also below.)

Determination

OXIDATION–REDUCTION REACTIONS

By far the most widely used analytical reaction for hydrazine involves its oxidation; this is of particular importance since ammonia, one of its decomposition products, does not interfere. For this purpose almost all the usual and a number of unusual oxidizing agents have been studied. Most procedures are suitable for mg.-quantities of hydrazine and use 0·1 N. solutions of reagents; except where otherwise stated they are not specific for hydrazine in the presence of hydroxylamine.

Potassium iodate has been used for the direct titration of hydrazine in acid solution, with chloroform for easy recognition of the end point[17, 18, 19] with Amaranth, Brilliant Ponceau 5R, or Naphthol Blue Black as indicator[20] or potentiometrically.[21] It has also been used in the back titration method, the excess being determined by titration with bisulphite[22, 23] or by the amperometric dead stop method with As^{3+} in presence of mercuric chloride,[24] after elimination of the iodine liberated in the hydrazine oxidation. This elimination can be avoided by adding mercuric perchlorate solution to the original reaction mixture to fix the liberated iodine.[25] Hydrazine can be determined in the presence of hydroxylamine by direct titration in acid solution containing 1–2% of sodium chloride with potassium iodate, destruction of the iodine cyanide with 0·1 N. sulphite solution and precipitation of the iodide with silver nitrate.[25, 26]

Potassium bromate gives better results in the direct[17] than in the indirect titration[23] of hydrazine and may be used with indigo,[17, 19] α-naphthoflavone,[27] or molybdenum blue[28, 29] as indicator.

Sodium hypochlorite can be used for the direct titration of hydrazine in acid solutions using indigo carmine or methyl red as indicator[30, 31]; in alkaline solutions special precautions are required to obviate errors due to atmospheric oxidation but the reaction can be used with phosphate buffers of pH 7 at 80° and with luminol as indicator.[32] The indirect titration in which excess of hypochlorite reacts with hydrazine at pH 7 (phosphate buffer), potassium iodide is added, the solution acidified, and the liberated iodine titrated with sodium thiosulphate,[23] can also be used. Chloramine T and Chloramine B can both be used in place of the less stable hypochlorite for these titrations. Chloramine T has been used for the direct titration in presence of sodium bicarbonate and potassium iodide to a starch end-point[33] or potentiometrically,[34] also in presence of iodine chloride as a catalyst and pre-oxidizer with chloroform for easy detection of the end-point.[35] The reaction conditions for Chloramine B are similar,[36–39] and in addition it has been used with potassium bromide in acid solutions as a bromometric agent in presence of indigo carmine indicator.[40]

Potassium permanganate may be used for the direct titration of hydrazine in hot hydrochloric acid solution,[19] in presence of potassium bromide, using Victoria Rubin or Naphthol Blue Black as indicator[41] or in the cold electrometrically.[42, 43] Titration in 0·1–1 N. sodium hydroxide solutions is reported to be satisfactory in presence of telluric acid[44] and in 0·75–1 N. sodium hydroxide solutions in presence of Ba^{++}; back titration procedures in which the excess of potassium permanganate is titrated with Tl^{+} are useful.[45]

After reaction with hydrazine in alkaline solution and acidification, excess of potassium permanganate may be determined also with sodium thiosulphate solution[19] in presence of potassium iodide.

Iodine chloride may be used for the direct titration of hydrazine either potentiometrically in acid or alkaline (bicarbonate or acetate buffered) solutions or visually with starch as indicator.[46] The use of iodine appears to be somewhat less satisfactory because of the instability of the reagent[17] and the slowness of the final stages of the reaction,[19] although it gives satisfactory results if special precautions are taken.[18] Some of the disadvantages are overcome by a back titration method when the excess of iodine is determined with thiosulphate.[19] A novel use of iodine in the determination of dilute solutions (10^{-5} M.) of hydrazine is in the polarization titration method of Franck.[47]

Other normal oxidation reagents which have been applied to the direct volumetric determination of hydrazine include (*a*) ceric sulphate in presence of potassium bromide[42]; (*b*) a stable complex of ceric sulphate, diethylenetetra-ammonium sulphato-cerate, which has been used in acid solution in presence of iodine chloride and chloroform for end-point detection[48]; (*c*) potassium metaperiodate, which reacts quantitatively with hydrazine in presence of concentrated hydrochloric acid[49] and may be used for its direct titration potentiometrically[50, 51] in presence of Br^{-}, using either iodine bromide and carbon tetrachloride for the visual detection of the end-point[52] or starch indicator in presence of potassium cyanide, sodium chloride, and hydrochloric acid[53]; and (*d*) selenious acid, which quantitatively oxidizes hydrazine under reflux in acid solution, the excess of selenious acid being measured iodometrically or by precipitation of selenium.[54]

Potassium ferricyanide has been used for the direct potentiometric determination of hydrazine in 10–25% potassium hydroxide[55] or to a colorimetric end-point measured with a Hilger Spekker absorptiometer in presence of osmium tetroxide catalyst.[56, 57] A back titration procedure in which excess of ferricyanide is titrated with standard Ce^{4+} in acid solution, with or without ferric chloride indicator, has also been described.[58]

Sodium metavanadate can be used for the direct titration of hydrazine in hydrochloric acid solution using iodine chloride and chloroform for the detection of the end-point.[59, 60] Sodium vanadate however can be used only in an indirect titration method in which at least a 50% excess of sodium vanadate in sulphuric acid solution is used, the excess being determined, after boiling, either with potassium permanganate in the hot or with Mohr salt in the cold solution.[61]

Two interesting reactions are the potentiometric determinations of hydrazine or hydroxylamine with ammoniacal copper sulphate at 90° using either bright platinum foil or copper as indicator electrode against a standard calomel cell preferably under nitrogen,[62] and of hydrazine or hydrazides with perchloric acid in glacial acetic acid solutions containing 1% mercuric acetate.[63] Hydrazine can also be titrated potentiometrically with *N*-bromosuccinimide in hydrochloric acid[64] and with sodium nitrite in hydrochloric, perchloric, or phosphoric acid solutions.[65]

The oxidation of both hydroxylamine and hydrazine is possible at a dropping mercury electrode in alkaline solution[66] and the electrolytic oxidation at 60–65° of hydrazine, in presence of potassium bromide and hydrochloric acid, to nitrogen with a coulometer in the circuit; on complete oxidation of the hydrazine bromine is liberated, and the silver precipitated in the coulometer at this point, corrected for the bromine liberated, is a measure of the hydrazine present.[67]

Finally there are oxidation procedures involving the liberation and measurement of nitrogen which are of particular use for determining hydrazine in the presence of hydroxylamine. A mixture of hydrazine and hydroxylamine is oxidized with excess of potassium bromate in 6 N. hydrochloric acid solution, in a closed system under carbon dioxide, the nitrogen liberated is collected over 50% potassium hydroxide and is a measure of the hydrazine present, while the bromate used (estimated by back titration with sodium thiosulphate) measures the hydrazine and hydroxylamine together.[68] Similarly hydrazine may be oxidized to nitrogen with cuprammonium salts; hydroxylamine does not interfere and may be determined by reduction to ammonia with ferrous sulphate.[69] In mineral acid solutions cupric oxide or manganese dioxide and potassium iodate also quantitatively oxidize hydrazine to nitrogen.[70, 71, 72]

ACID–ALKALI TITRATIONS

Since hydrazine is a weak base it can theoretically be determined by titration with acid, and in fact this is the basis of several published analytical methods. Free hydrazine gives an electrometric curve corresponding to that of a mono-acidic base while titration curves of hydrazine salts show two inflexions, the first of which is sharp enough for practical use.[73] Unfortunately hydrazine usually contains ammonia as a decomposition product which interferes with the acidimetric though not with the oxidimetric titration; and it has therefore been recommended that ammonia and hydrazine be determined together acidimetrically either directly with hydrochloric acid[74] or by back titration of excess of acid with sodium hydroxide[75] while the hydrazine alone is determined oxidimetrically. Hydrazine sulphate may however be titrated, either potentiometrically or visually using Methyl Orange as indicator, with sodium hydroxide, barium hydroxide, and sodium carbonate.[76] An ingenious combined oxidimetric-acidimetric method[77] involves reaction of hydrazine sulphate with bromine according to the equation:

$$N_2H_4{,}H_2SO_4 + 2Br_2 \rightarrow N_2 + 4HBr + H_2SO_4$$

and titration of the acid liberated by the ferrocyanide method; hydroxylammonium chloride reacts similarly.[77]

KJELDAHL REACTIONS

The variation in the ease of liberation of ammonia from ammonium salts and from hydrazine makes possible their determination in the presence of one another by Kjeldahl methods. Reduction of hydrazine is achieved with hydriodic acid,[78] or hydriodic acid and phosphorus[79] either under reflux or in a sealed tube; but a selenium–perchloric acid mixture will not effect the reduction.[80] If a mixture of hydrazine and ammonium salts is treated with sodium hydroxide and excess of potassium permanganate, the hydrazine is oxidized to nitrogen but the ammonium salt is unchanged and may be determined by Kjeldahl distillation.[81] Similar pretreatment of the sample in hydrochloric acid solution, with excess of potassium iodate and aspiration of the solution oxidizes and removes the hydrazine before Kjeldahl determination of the ammonium salt.[82]

COLORIMETRIC DETERMINATIONS

Colour reactions are of particular use in determining small quantities of hydrazine in organic amines and azides and may also, where suitable, be used merely for the detection of hydrazine. The intensely red-orange azine of *p*-dimethylaminobenzaldehyde is stable in acid solutions and measurement of its absorption intensity at 458 mμ, where Beer's Law is obeyed, permits determination of μg.-quantities of hydrazine with an accuracy within 1–2%[83, 84]; this method has been satisfactorily applied to the determination of traces of hydrazine in sodium azide[85] and in water.[86] The brown complex formed with picryl chloride in chloroform after the addition of potassium acetate and ethanol can also be determined photometrically and is of use in determining less than 30 p.p.m. of hydrazine in dilute solutions.[87] Finally, mg. quantities of hydrazine may be determined by cold potassium dichromate in 14 N. sulphuric acid; comparison of the absorption of the solution at 590 mμ with a standard curve indicates the amount of hydrazine present.[88]

Purity of Hydrazine

Traces of impurities in hydrazine are principally detected and determined by physical methods. Water may be determined by infra-red spectrophotometry using the absorption band of water, 1·9 μ,[89] by high-frequency oscillation,[90] or in larger concentrations by the Karl Fischer method[91] or refractometrically,[92] while infra-red spectroscopy is of value in detecting, identifying, and in many cases determining a large number of gases and vapours which may contaminate hydrazine.[93] The *X*-ray powder-patterns of chloroplatinates of amines prepared by distillation in a micro-gas cell into a hanging drop of chloroplatinic acid permits the identification of a large number of such amines.[94]

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ORGANIC REACTIONS OF HYDRAZINE

Hydrazine undergoes the wide range of organic reactions[1] that may be expected of the simplest diamine, although the reactivity is modified somewhat by the close proximity of the two reactive centres. Here only the primary reactions of hydrazine itself are discussed; some further reactions of the products and of substituted hydrazines have been reviewed elsewhere.[1]

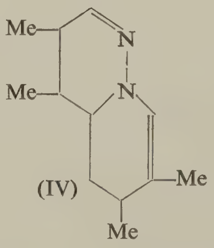
ADDITION REACTIONS

Hydrazine adds to certain multiply-bonded functional groups, either with or without subsequent elimination of water. Whereas no reaction has been reported with simple olefines, hydrazine adds to activated ethylenic systems; with acrylonitrile mono- or di-addition is possible[2] giving (2-cyanoethyl)hydrazine (I) and di-(iminopropionitrile) (II), respectively. Addition to a conjugated di-olefine occurs[3] in presence of alkali metals; butadiene gives *NN*-dicrotylhydrazine (III) (or nitrogen-rich polymeric material) and 2,3-dimethylbutadiene gives a high yield of the cyclized product (IV).

$NH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ (I)

$({\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CN)_2$ (II)

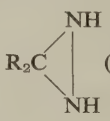
$(CH_3{\cdot}CH{:}CH{\cdot}CH_2)_2{:}N{\cdot}NH_2$ (III)



(IV)

$R_2C{:}N{\cdot}NH_2$ (V)

$R_2C{:}N{\cdot}N{:}CR_2$ (VI)

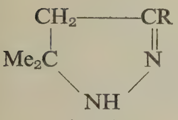


(VII)

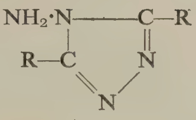
With simple carbonyl compounds, such as aldehydes and ketones, condensation occurs with formation of a C═N group, usually, either of the hydrazone (V) or of the azine (VI) system; in special conditions *iso*hydrazones (VII) may be formed. Whether the hydrazones or azines are formed depends on the relative rate of their interconversion, on the presence or absence of an acidic catalyst,[4] and to some extent on the solubilities of the products and proportions of reagents. Aldehydes react faster with the hydrazone than with hydrazine, and the azine (VI) is the normal product. Ketones react more slowly and the presence of an excess of ketone is desirable if the azine formation is to be assured; otherwise the hydrazone is normally isolatable. The cyclic *iso*hydrazones of type (VII) have been recognized recently[5] as the products of the reaction of ketones with hydrazine generated *in situ* from ammonia and chloramine; alternatively they may be regarded as the products of addition of chloramine to the imine $R_2C{=}NH$.

All these carbonyl derivatives are hydrolysed by hot dilute mineral acid,[6] when the starting materials are regenerated. This forms the basis of several isolation procedures, both of carbonyl compounds and of hydrazine. The hydrazones and azines undergo a variety of oxidation and reduction reactions which have been reviewed[1] and are of some industrial importance.

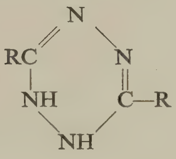
Finally in strongly acidic solution a fourth reaction, namely the formation of a pyrazoline, is possible[7] between ketones (in excess) and hydrazine. This cyclization involves both addition to and substitution of (the enolic form of) the ketone, and acetone gives (VIII).



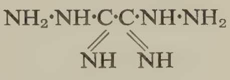
(VIII)



(IX)



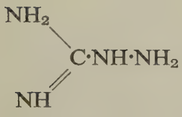
(X)



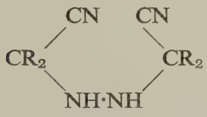
$NH_2{\cdot}NH{\cdot}\underset{NH}{C}{\cdot}\underset{NH}{C}{\cdot}NH{\cdot}NH_2$

(XI)

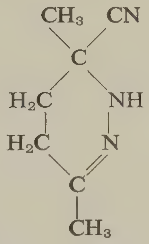
With nitriles, addition across the triple bond occurs[8] with formation of a new C–N linkage; the usual product from organic cyanides is a 4-amino-1,2,4-triazole (IX) though in anhydrous conditions the precursor (X) in the dihydrotetrazine series may be isolated. In suitable circumstances open-chain addition products are formed; thus cyanogen gives[9] the di-adduct (XI), the mono-adduct being isolated in special conditions only. The reaction of hydrazine with cyanamide ($NH_2.C{\equiv}N$) gives aminoguanidine (XII),[10] a valuable intermediate for photographic chemicals, also obtained[11] by the action of hydrazine on nitroguanidine.



(XII)



(XIII)



(XIV)

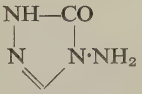
It is noteworthy that hydrazine does not attack the nitrile group of ketone cyanohydrins,[12] but gives α-hydrazino-nitriles (XIII) made up of two ketone residues for each hydrazine residue; the 1:1 product cannot normally be isolated.

With the cyanohydrin of a 1,3-diketone, on the other hand, hydrazine affords[13] 3,6-dimethyl-2,3,4,5-tetrahydro-3-cyanopyridazine (XIV).

Hydrazine adds to CO_2 and CS_2 to give aminocarbamic acid or its hydrazine salt and the corresponding dithiocarbazinate (XV) respectively[14]; the latter is readily converted into thiocarbohydrazide by loss of H_2S. Addition to cyanic acid affords[15] either semicarbazide or dehydrourea (hydrazoformamide) (XVI), the latter being a valuable starting material for azoformamide, a blowing agent in wide use. Thiocyanic and selenocyanic acid undergo[16] analogous reactions.

$NH_2{\cdot}NH{\cdot}CS{\cdot}SH,N_2H_4$ (XV)

$NH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$ (XVI)



(XVII)

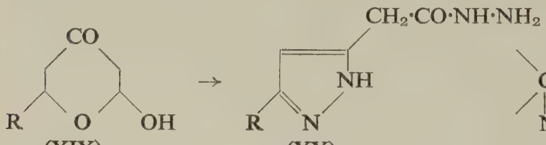
$HO{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}NH_2$

(XVIII)

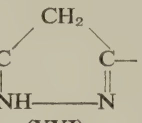
With CO, hydrazine first gives $CO(NHNH_2)_2$ which under the vigorous reaction conditions[17] cyclizes to 4-amino-1,2,4-triazol-3-one (XVII).

Hydrazine not only adds to multiple bonds, but also reacts[18] with epoxides. Typically, with ethylene oxide it gives 2-hydroxy-ethylhydrazine (XVIII), a valuable intermediate in pharmaceuticals manufacture. $\alpha\beta$-Epoxycinnamyl alcohol gives[19] 3-hydrazino-3-phenylpropane-1,2-diol.

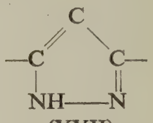
With lactones the hydroxy-hydrazide of the acid is obtained,[20] but pyrones (XIX) undergo[21] condensation at the carbonyl group as well as suffering opening of the lactone ring; the product is a pyrazole derivative (XX).



(XIX) (XX)



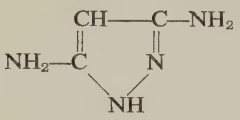
(XXI)



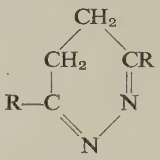
(XXII)

Compounds containing two centres to which hydrazine may add readily form cyclic systems. The $\alpha\beta$-unsaturated carbonyl compounds afford[22] pyrazolines (XXI) as discussed by Wieland (Mellor, VIII, 309) whereas acetylenic ketones or aldehydes give[22] pyrazoles (XXII).

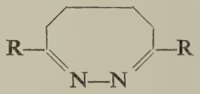
Malonitrile with hydrazine forms a pyrazole (cf. Ref. 8), the diamino-compound (XXIII).



(XXIII)

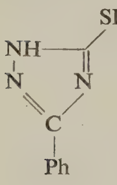


(XXIV)

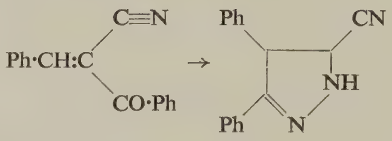


(XXV)

Pyrazoles are also obtained[23] from 1,3-diketones or β-keto-aldehydes or their bis-acetals.[24] With 1,4-diketones the corresponding six-membered dihydro-pyridazine system (XXIV) is favoured[25] though by-products are often encountered.[26] 1,6-Diketones, e.g., 1,4-dianisoylbutane, afford 4,5,6,7-tetrahydro-1,2-diazocines[27] (XXV).



(XXVI)



(XXVII) (XXVIII)

$Ph{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}COR$

(XXIX)

The action of hydrazine on benzoyl*iso*thiocyanate, Ph.CO.NCS, gives[28] 3-phenyl-1,2,4-triazole-5-thiol (XXVI).

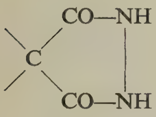
Reactions with hydrazine of molecules containing three reactive centres have also been studied; thus α-benzoylcinnamonitrile (XXVII) yields[29] the pyrazoline (XXVIII), the cyanide grouping remaining unattacked; but when the system is (XXIX) the pyrazole ring is formed[30] between the original carbonyl carbon atoms to give a 3-styryl-pyrazole.

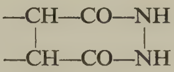
SUBSTITUTION REACTIONS

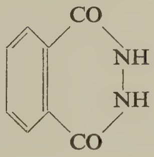
In substitution reactions hydrazine behaves as a typical amine, but it is more basic than ammonia. It reacts with alkyl halides and activated aryl halides. Isolation of pure mono-alkylhydrazine is made difficult by the fact that these substances react more rapidly with the halide than does hydrazine itself; from simple halides, therefore, a mixture of mono-alkyl and *NN*-dialkyl derivatives is obtained.[31] A good illustration is the fact that di-(2-chloroethyl) ether with hydrazine gives[32] 4-aminomorpholine and not a linear polymer.

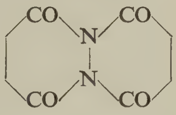
With amides or esters (or if necessary acyl chlorides, and acid anhydrides) acyl hydrazides are formed.[33] These hydrazides retain the ability to condense with carbonyl compounds and the acyl group may be removed again hydrolytically and thus used as protecting group for one of the NH_2 groups of the hydrazine molecule.

With malonic esters[34] cyclic hydrazides, pyrazolidine-3,5-diones (XXX) are formed. From 1,2-dicarboxylic acids, cyclic hydrazides, 1,2,3,6-tetrahydropyridazine-3,6-diones (XXXI) are obtained: maleic hydrazide has already been mentioned (see page 96); phthalic hydrazides, too, are well known.[35] Phthalic hydrazide (XXXII) is also formed as a by-product in the reaction of phthalimides with aqueous hydrazine (Ing-Manske modification of Gabriel's synthesis). Hydrazine has been found to react with a number of heterocyclic 1,2-di-acids[36] and the cyclic hydrazides resulting represent complex heterocyclic systems.


(XXX)


$$\begin{array}{l}—CH—CO—NH\\ \quad| \qquad\qquad |\\ —CH—CO—NH\end{array}$$
(XXXI)


(XXXII)


(XXXIII)

Succinic acid derivatives often give mixtures[37]; among a variety of compounds obtained from succinic anhydride[38] are the cyclic hydrazide and the bis-compound (XXXIII). *N*-Carboalkoxyl-α-amino-acid esters also give cyclic hydrazides,[39] namely 1,2,4-triazines. Esters of long-chain dibasic acids, *e.g.* sebacates, may be converted into linear polymeric hydrazides which are of some interest as fibre-forming materials.

Sulphonyl halides similarly[40] give sulphonhydrazides, several of which are manufactured as blowing agents or free-radical initiators. Organo-phosphoric acid hydrazides have also been described.[41]

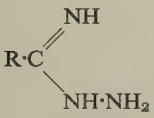
Urea or thiourea or substituted derivatives react with hydrazine as typical mono-amides, giving semicarbazide or thiosemicarbazide, but in presence of excess of urea, hydrazoformamide (XVI) is obtained[42] in high yield. Because of their potential pharmaceutical interest, thiosemicarbazides have been prepared in large numbers.

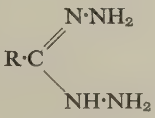
Carbohydrazide, $CO(NH.NH_2)_2$, is not directly accessible from urea but may be obtained from carbon monoxide and hydrazine under pressure (see above); it is best prepared from carbonic esters, especially diphenyl carbonate[43] or from phosgene.[44] Surprisingly,[45] carbonyl cyanide affords $(NH.CO.CN)_2$.

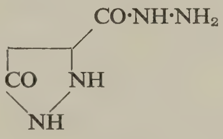
Similar substitution of hydrazine for cyano grouping occurs[46] in the reaction with tetracyanoethylene, which yields *NN'*-di-(1,2,2,-tricyanoethenyl)hydrazine.

Hydrazine reacts with substituted carbamoyl chlorides, $R_2N.CO.Cl$, giving[47] the expected hydrazide $R_2N.CO.NH.NH_2$ when R is aromatic, but the *NN'*-disubstituted hydrazine is formed when R is alkyl.

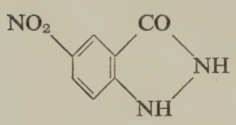
With imino-ethers[48] the mono-(XXXIV) or di-substitution products (XXXV) may be obtained:

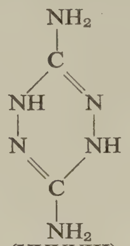

(XXXIV)

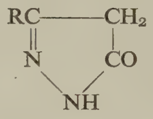

(XXXV)

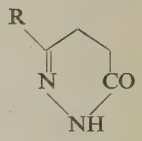

(XXXVI)

Normally, when two reactive centres are present in the molecule, double substitution with or without cyclization occurs. This is clearly so for molecules containing two isolated halogen atoms,[49] and the reactions of di-esters have already been noted. Halogeno-esters may form[50] the hydrazino-ester, hydrazino-hydrazide or cyclic systems with five or six members: thus halogenosuccinates yield[51] pyrazolid-3-ones (XXXVI) carrying a hydrazidocarbonyl substituent in the 5-position; the same reaction is encountered[52] in activated aromatic systems when ethyl 2-chloro-5-nitrobenzoate affords 1,2-dihydro-5-nitroindazol-3-one (XXXVII).


(XXXVII)


(XXXVIII)


(XXXIX)

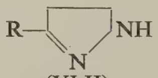

(XL)

Pressure-reaction of ethyl carbamate and hydrazine proceeds with doubling of the molecule[53] and gives (XXXVIII).

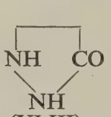
REACTIONS INVOLVING BOTH ADDITION AND SUBSTITUTION

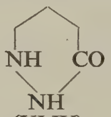
In molecules containing isolated reactive centres, hydrazine can be introduced at each centre; this has been discussed above for both additive and substitutive reactions. The greatest interest usually attaches to molecules in which these centres are at a distance of three or four carbon atoms, since heterocyclic systems with five- or six-membered rings and two adjacent nitrogen atoms result. Thus β-keto-esters readily yield[54] pyrazol-3-ones (XXXIX), and γ-keto-esters analogously[55] give the pyridazones (XL). An interesting special case is that of Mannich bases[56] (XLI) when, besides hydrazones or azines, the pyrazoline (XLII) may be formed by replacement of the terminal dialkylamino group.

$R\cdot CO\cdot CH_2\cdot CH_2\cdot NR'_2 \rightarrow$ (XLI)


(XLII)

Simultaneous addition and substitution also occurs[57] in acetylenic and olefinic esters, (substituted) acrylates giving pyrazolidones (XLIII). Ethyl cinnamate thus gives[58] 3-phenyl-5-pyrazolidone and substituted cinnamates behave analogously.[59]


(XLIII)


(XLIV)

$\beta\gamma$-Unsaturated esters give the corresponding pyridazone (XLIV); the corresponding acetylenic esters analogously give the pyrazolones and pyrazones.

HYDRAZINE AS OXIDIZING AND AS REDUCING AGENT

Although hydrazine[63] is best known as a reducing agent, it does at times cause oxidation, being itself reduced[60] to ammonia. For instance, glycollic acid is oxidized to oxalic acid,[61] and formaldehyde or formic acid is oxidized to carbon dioxide. Cellulose, too, reduces hydrazine to ammonia.[62] One particularly well known reaction is the formation of osazones from aldoses, which involves the oxidation of a secondary alcohol group to carbonyl.

More commonly, however, hydrazine behaves as a powerful reducing agent both by itself and in presence of noble metal catalysts. The reduction of carbonyl compounds by the Wolff–Kishner process[62] is often used for acid-labile materials and has more recently been much improved.[64]

In the presence of traces of oxidizing agent hydrazine reacts with olefines, saturating the double bond. Hydrazine reacts also with unsaturated fatty acids,[65] oleic giving stearic acid; the glycerides can also be hardened in mild conditions[66] with the additional advantage that excess of the reducing agent is readily removed as ammonia gas. The presence of palladium accelerates the process,[67] and also permits the reduction of stilbene to 1,2-diphenylethane.

Aromatic and other nitroso- or nitro-compounds afford[68] amines in high yield, other functional groups being unaffected, but in special conditions azoxy-[69] or hydrazo-compounds[70] may be isolated, possibly as intermediates. Analogously nitrate esters are reduced,[71] giving mixtures of reduction products of different oxidation states.

Hydrazine replaces certain activated halogeno atoms by hydrogen, for instance those in α-halogeno esters[72] or in activated aromatic systems.[73]

Finally hydrazine reduces quinones to hydroquinones.[74]

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TETRAFLUOROHYDRAZINE

Tetrafluorohydrazine, N_2F_4, was added[1] to the known binary compounds of nitrogen and fluorine in 1958.

PREPARATION

Tetrafluorohydrazine is prepared by the reaction of nitrogen trifluoride with metals, according to the equation

$$2NF_3 + M \rightarrow N_2F_4 + MF$$

Metals used were[1] stainless steel, copper, arsenic, antimony and bismuth and in a flow reactor at 375° (residence time 13 min.) the yield was between 60 and 70% of the theoretical (40 to 60% conversion).

SPECTRAL DATA

The infra-red absorption spectrum of tetrafluorohydrazine has[1] a very strong complex band between 9·75 and 10·75 μ and a strong band at 13·6 μ. The mass-spectroscopic fragmentation pattern has been reported,[1] and the n.m.r. spectrum consists[1] of one broad unresolved band at a field approximately 75 p.p.m. lower than that of the ^{19}F nuclei of trifluoroacetic acid.

PHYSICAL PROPERTIES

Tetrafluorohydrazine is calculated[1] to boil at −73° and has a heat of vaporization estimated as 3·17 kcal. per mole. The critical temperature is 36° and the critical pressure 77 atm. The vapour pressure–temperature relation can be expressed by the Clausius–Clapeyron equation:

$$\log P = -692/T + 6{\cdot}33$$

when the pressure P is expressed in mm. Hg.

HAZARDS

In presence of oxygen, tetrafluorohydrazine admixed with organic materials is likely to explode.[3]

CHEMICAL PROPERTIES

As might be expected from its low N–N bond strength,[2] tetrafluorohydrazine participates readily in free-radical reactions. In a glass vessel with chlorine under u.v. irradiation it gives[3] chlorodifluoroamine, $ClNF_2$, in an equilibrium reaction favoured by a large excess of chlorine and a relatively high temperature (namely 80°). The photolysis of diketones in presence of tetrafluorohydrazine yields[3] *NN*-difluoroamides, also obtained from aldehydes at 150°:

$$\mathrm{RCO.COR + N_2F_4 \rightarrow 2RCO.NF_2}$$
$$\mathrm{R.CHO + N_2F_4 \rightarrow R.CO.NF_2 + HNF_2}$$

With alkyl radicals, generated either from alkyl iodides[4] or by decomposition[3] of aliphatic azo-compounds or of hexaphenylethane, tetrafluorohydrazine affords the corresponding stable substituted difluoroamine.

Tetrafluorohydrazine on heating abstracts hydrogen from mercaptans, thiophenols, or arsine and gives difluoroamine, NHF_2; yields are high, 74% with thiophenol at 50° and 52% with arsine at 50° being reported.[5]

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SECTION XXI

HYDROXYLAMINE

BY K. G. MASON

PREPARATION

Raschig's Synthesis

Several variations of the original Raschig synthesis of hydroxylamine (from sodium nitrite and sulphite or bisulphite and sulphur dioxide) have been published, largely in the patent literature. Thus, aqueous ammonium nitrite and ammonium sulphite are treated with gaseous sulphur dioxide below 0°; after hydrolysis and neutralization a solution containing 5·48% of hydroxylamine is obtained.[1] Yields of 89·5% and 89·7% are claimed when sulphur dioxide is passed into an aqueous mixture of (i) ammonium nitrite, carbonate and bicarbonate at $-3°$ until pH 2 is attained, or (ii) ammonium nitrite, nitrate and carbonate until it is faintly acid.[2, 3] A continuous process is also described in which an aqueous solution of ammonium nitrite and carbonate is circulated through a packed column, 10% sulphur dioxide in an inert gas being introduced at the bottom at such a rate as to maintain pH 2–2·5 in the solution; a portion of the solution is continuously drawn off and processed to give aqueous hydroxylammonium sulphate. The solutions of ammonium nitrite containing carbonate and bicarbonate can be prepared[4] by burning an ammonia–air mixture over a Pt–Rh grid and leading the gases into aqueous ammonium bicarbonate. A mixture of nitric oxide and nitrogen dioxide is produced when ammonia is burned in air over a catalyst[5, 6]; the cooled mixture is caused to react[5] with aqueous ammonium sulphite in a tower at pH 9 and 6°. Further cooling and treatment with sulphur dioxide and ammonium sulphite to pH 3·3 complete the disulphonation. Hydrolysis of the disulphonate gives hydroxylammonium sulphate in 63·4% overall yield on the ammonia burned. Another continuous process[7–10] involves the reaction between a mixture of alkali metal, alkaline-earth or ammonium nitrite, and bisulphite, hydroxide or salts which give bisulphites with sulphur dioxide, and sulphur dioxide in a counter-current process; considerable emphasis is attached to the control of the pH. Alternatively[11] sulphur dioxide is fed rapidly into a vigorously stirred aqueous solution of nitrites and bisulphites at a low temperature; the rapid feed and low temperature prevent hydrolysis before the reaction is complete. Other patents describe the use of ammonium salts,[12, 13] alkali metal salts[14] or calcium salts.[15–19] In the last case the initial reaction below 10° produces calcium hydroxylamido-*N*,*N*-disulphate which is then hydrolysed to hydroxylammonium sulphate at 80–100°. The use of the potassium salts, with isolation of the potassium hydroxylamido-*N*,*N*-disulphate followed by hydrolysis, gives greater yields (85%) than the use of the sodium salts (50%).[20] The presence of a sulphide of an alkali or alkaline-earth metal is claimed to increase markedly the yield of hydroxylamine from the hydrolysis of hydroxylamido-*N*,*N*-disulphate.[21] The optimal conditions for the preparation of hydroxylamine by Raschig's method have been re-investigated.[22] The conclusion reached is that the best procedure is that in which a mole ratio of 1:1·95 for $NaHSO_3:NaNO_2$ is used.[23] The heat of hydrolysis of the intermediate disulphate has been utilized to maintain the reaction.[24, 25] A 92% yield results from the addition of slightly less than one molecular equivalent of liquefied sulphur dioxide to aqueous sodium nitrite and bisulphite (each molar) below 0°, followed by five hours boiling.[26–28] The reaction of acetone with sodium hydroxylamido-*N*,*N*-disulphate (formed by reaction between sodium nitrite, sodium bisulphite and sulphur dioxide) gives acetoxime,[29] which yields 70% hydroxylammonium chloride when distilled with hydrochloric acid.

The mechanism of the Raschig synthesis has been investigated by means of specially developed analytical techniques.[30] Raschig's theory of the intermediate formation of dihydroxylamidosulphuric acid, $(HO)_2N.SO_3H$, and the compound $ONSO_3$ was not confirmed; probable intermediates were thought to be nitrous acid, HNO_2, and the nitrosyl ion, NO^+. The formation of hydroxylamine by the reaction of chloramine with water has been studied.[31]

Reduction of Nitric Oxide, Nitric Acid, etc.

Several patents have been published detailing various conditions for the hydrogenation of nitric oxide in acidic solution. The variations largely deal with the catalyst. Thus platinum,[32] platinum and carbon[33–35] or palladium[36] is used at 0–30° and 83% yields are claimed for a platinum catalyst at 40–60°[37]; at lower temperatures the yield drops markedly, e.g. to 4% at 5°. The efficiency of the catalyst is claimed to be enhanced by addition of a wide variety of substances; e.g., platinum containing 5% of gold or 1% of iridium is said to give 20–30% better yields than unalloyed platinum.[38] The addition of 5–15% of trivalent arsenic, antimony or bismuth, quadri- or bi-valent sulphur, selenium or tellurium increases the selectivity of platinum or gold catalysts, the yield of hydroxylamine increasing from 56·4–63·9% to 73·2–83·2%.[39–41] The addition of lead as nitrate or mercury as mercuric chloride is claimed to improve the yield, in presence of a platinum catalyst, from 62·6 to 78·5% and to 81·9%, respectively.[42] The addition of oxidizing agents[43] and of ammonium hydroxide, *iso*valeric acid, hexahydrobenzoic acid, dioxan, *cyclo*hexanone oxime or *cyclo*hexanol[44, 45] is also said to increase the catalyst efficiency. Nitrous acid solution, prepared[46] by the addition of a mineral acid to an aqueous or aqueous-alcoholic solution of an alkali-metal nitrite, can be hydrogenated under pressure in the presence of a platinum metal to give hydroxylamine.

The catalytic reduction of nitro-urea to hydroxylammonium salts, semicarbazide salts and mixtures of the two has been described.[47] Hydrogenation of nitric acid in the presence of a catalyst consisting of platinum or rhodium on active carbon gives hydroxylamine, ammonia and nitrogen.[48, 49] If alumina is used as the carrier or copper is added to the catalyst, its efficiency is reduced and less ammonia is formed; and in the presence of palladium, palladium oxide, platinum or platinum oxide and sulphuric or phosphoric acid a 35% conversion into hydroxylamine without the formation of any ammonia is claimed.

The electrolytic reduction of nitric acid to hydroxylamine is described in several patents. In the majority of cases a mercury cathode is used with various anodes. Sulphuric acid[50–52] or hydrochloric acid[53–58] is added to the nitric acid as catholyte. In the latter case the catholyte is usually withdrawn on completion and hydroxylammonium chloride precipitated by the passage of dry hydrogen chloride into the cooled solution. As anode the use of lead dioxide,[56, 58] graphite[57] or lead[52] is recommended. The use of a ferric oxide anode with a lead–mercury amalgam in a lead container as cathode has been described.[59] In this process nitric acid is added dropwise to a hydrochloric acid catholyte, the anolyte also being hydrochloric acid; similarly, lead dioxide may be used as anode and sulphuric acid as the anolyte.[60] An early paper[61] described the direct preparation of hydroxylamine from sodium nitrate by electrolysis in sulphuric acid solution. The hydroxylamine was isolated as a benzene solution of acetoxime, which was hydrolysed by shaking the solution with 25% hydrochloric acid; the solution of hydroxylamine hydrochloride was separated and evaporated to dryness. The electrolytic reduction of nitric acid using sodium amalgam as the reducing agent has been described[62]; a mercury cathode is used, with 10% aq. sodium sulphate as the electrolyte and thorium and iron salts or urea as catalysts. An oscillographic study[63] of the activation and subsequent repassivation of iron in nitric acid by the passing of a current shows that at the minimum in the voltage–time curves the iron surface is free from the passive layer, iron is dissolving, hydrogen is being evolved and nitric acid is being reduced to nitrous acid, hydroxylamine, ammonia and nitrogen; the voltage then rises to a plateau and the sole reduction product is nitrous acid. A polarographic study[64] of the reduction of nitrate ions in the presence of La^{3+} or Ce^{3+} ions indicates that hydroxylamine and ammonia are produced in equal amounts. At a large mercury cathode the reduction of nitrate ion in the presence of uranyl ion gives predominantly hydroxylamine, whilst the presence of lanthanum or cerium leads to ammonia and hydroxylamine as the chief products.[65] The same workers observed that in an acidic medium, without any specific catalyst, polarographic reduction of nitrate ion gives nitrite ion as the major product. The polarographic reduction of nitrous acid in unbuffered[66] solutions and in buffered[67] solutions of low pH gives hydroxylamine. At pH values greater than 4·22 (acetate buffer) a second wave, half the height of the first, is observed which is due to the further reduction of the hydroxylamine to ammonium hydroxide. In a general survey[68] of the choice between diaphragm and amalgam- or mercury-cell processes, hydroxylamine is mentioned in a list of compounds that can be made from alkali metal amalgams formed in mercury cells.

Electrochemical methods for the formation of hydroxylamine have been reviewed.[69]

Oxidation of Ammonia

The oxidation of ammonia by oxygen over a platinum catalyst has been investigated at 1140°, 1250° and 1350°.[70] Various molar ratios were used and it was demonstrated that, if the products are condensed immediately, hydroxylamine, nitrous acid, ammonia and traces of hydrazine can be isolated. If however the condensation is delayed, more nitrous acid is isolated at the expense of the hydroxylamine. It is concluded that the nitrous acid is produced at least partly in the gas phase and not on the surface of the catalyst; also hydroxylamine appears to be a primary decomposition product and is not formed by a wall reaction. The mechanism of the catalytic oxidation of ammonia has been extensively investigated by other workers[71, 72] who concluded that the primary reaction is:

$$NH_3 + O \rightarrow NH_2OH$$

Schemes were also given for the subsequent formation of nitrous acid, peroxonitric acid, nitric oxide, hyponitrous acid, nitrous oxide and nitrogen. Hydroxylamine is formed when activated charcoal, saturated with ammonia, is exposed to the air.[73]

In the oxidation of ammonia, in aqueous solution, by ozonized oxygen it was found that the formation of hydroxylamine is the first and rate-determining step of the whole process. Various compounds were examined for their value as catalysts and it was shown that Cu^{++} ions are more efficient than either Co^{+++} or Ni^{++} ions.[74]

Decomposition of Aliphatic Nitro-Compounds

Several different methods have been published for the preparation of hydroxylamine from aliphatic nitro-compounds, some of which provide the best and most economical routes to hydroxylamine. When nitromethane is heated with sulphuric acid at 100–110° the products consist of carbon monoxide, carbon dioxide, ammonia and hydroxylamine.[75] A similar method[76] claims that primary nitroparaffins yield a carboxylic acid and hydroxylammonium chloride when refluxed with constant-boiling hydrochloric acid; for example, when 1-nitropropane is refluxed with constant-boiling hydrochloric acid, using propionic acid as solvent, for 24 hours an 88% yield (allowing for recovery of starting material) of hydroxylammonium chloride is obtained. Another process[77] recommends the use of iron-free 95% sulphuric acid at a temperature of 120–130°. The product is obtained in a neutral and chemically pure state by precipitation from a small amount of water by the addition of ethanol. The preparation of hydroxylammonium chloride was also investigated, a longer reaction time being found necessary. The yield of hydroxylammonium salts from lower

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primary nitroalkanes and sulphuric acid at reflux temperatures is improved by the addition of a small amount of ferrous ammonium sulphate.[78] By keeping the iron content below 0·005 wt.-% an increase in yield from 87 to 94·5% is claimed.

Hydroxylammonium salts can be prepared in high yield by heating 1,2-dinitroethane, prepared from ethylene and dinitrogen tetroxide, with a mineral acid other than nitric acid or similar oxidizing acids.[79, 80] The use of concentrated sulphuric acid[81–83] at 100° is safer than the earlier method using hydrochloric acid at 150°, and is claimed to be more economical than the classic Raschig method. Nitroalcohols, $R_2C(NO_2)CH_2OH$, are decomposed by sulphuric acid into ketones, R_2CO, carbon monoxide and hydroxylamine[84]; hydroxylammonium sulphate can be isolated from the liquor when the evolution of carbon monoxide ceases.

The condensation of nitromethane with an aldehyde such as benzaldehyde yields a product which can be hydrolysed by hydrochloric acid at 100–125° to form an acid and hydroxylammonium chloride.[85]

The action of hydrochloric acid on nitroethylene has been reported to yield hydroxylammonium chloride.[86] This reaction has been investigated more thoroughly and several α-nitro-olefines were examined.[87] The reaction is said to proceed via 1,2-dichloronitroso compounds to 1,2-dichloro-oximes, if an α-hydrogen atom is present; hydrolysis by water then gives hydroxylammonium chloride and an α-hydroxy- or α-chloro-carboxylic acid. The yields are sometimes better with anhydrous hydrogen chloride, e.g. 90% from nitroethylene, and sometimes better with concentrated hydrochloric acid, e.g. 86% from 1-nitro-2-methylpropylene. In the absence of an α-hydrogen atom, e.g. 2-nitropropylene or 2-nitro-but-2-ene, the yield is either very low or zero.

Miscellaneous Processes

Irradiation of aqueous solutions of hydrogen azide[88, 89] with ultra-violet light results in the formation of hydroxylamine. It is supposed that the initial photolysis produces the imine radical HN:, which then reacts with the water present to form hydroxylamine. Hydroxylamine is also formed[90] by *X*-ray irradiation of adenine, guanine, cytosine, alanine, lysine, histamine and ethylamine but not of hypoxanthine, uracil, uridine and ammonia. The yield in the reactions varies with the pH.

The oxidation of sodium azide with sulphuric acid yields one-seventh of the amount of hydroxylamine demanded by the equation:

$$HN_3 + H_2O \rightarrow N_2 + NH_2OH$$

It was assumed[91] that the initial products are nitrogen and HN: and that the major portion of the latter is further oxidized to nitrogen, only a small amount reacting with the water present to form hydroxylamine.

An investigation[92] of the preparation of hyponitrites by the reduction of metallic nitrites and nitrates with magnesium amalgam revealed that in the preparation of the lithium, sodium, potassium, calcium, barium, strontium, zinc, cadmium and lead salts, hydroxylamine is present in the solution. This is not so with the rubidium and cæsium salts. The reduction of a mixture of nitric and sulphuric acids with the magnesium amalgam reagent affords a 60% yield, calculated on the nitric acid consumed, of hydroxylammonium sulphate.

The reduction of acetone with sodium nitrite and zinc dust gives a 95% yield of acetoxime which, heated with concentrated hydrochloric acid for fifteen hours on a water-bath, gives 98·9% of hydroxylammonium chloride.[93] The formation of an insoluble ketoxime can be used to recover hydroxylamine from aqueous solutions, and the hydroxylamine regenerated by hydrolysis.[94] Phosgene oxime is formed[95] by the chlorination of the reaction mixture produced by treating acetone with a mixture of nitric and hydrochloric acids. The phosgene oxime can be hydrolysed by boiling the solution, and evaporation then affords hydroxylammonium chloride.

The hydrolysis of an organic nitrite just below its decomposition point and treatment of the reaction products with hydrochloric acid gives hydroxylammonium chloride.[96]

Unsuccessful attempts[97] to prepare deuterohydroxylamine, D_2NOD, by successive exchanges of hydroxylamine with deuterium oxide resulted in a successful adaptation of Uhlenhuth's method[98] both for the preparation of anhydrous hydroxylamine, m.p. 32–33°, and of deuterohydroxylamine. An exchange with deuterium oxide of tri-hydroxylammonium phosphate gives trideuterohydroxylammonium phosphate and thermal decomposition, at 130°/13 mm., of the latter gives the required deuterohydroxylamine.

The formation of hydroxylamine is the first step in the hydrolysis of chloramine. However a second, and faster, reaction between hydroxylamine and chloramine also occurs[99]:

$$NH_2Cl + OH^- \rightleftharpoons NH_2OH + Cl^-$$

$$NH_2Cl + 2NH_2OH + OH^- \rightleftharpoons NH_3 + N_2 + 3H_2O + Cl^-$$

Hydroxylamine is said to be formed in traces by the prolonged contact of ether, containing peroxides, with ammonia. Small amounts of hydrazine are also formed.[100]

Aqueous solutions of free hydroxylamine are conveniently prepared from solutions of hydroxylammonium salts by ion exchange.[101, 102] Using the resin Wofatit L150 (OH form), it was found possible to prepare solutions of 7 M. concentration.[102] The prepared solutions are quite stable, a molar solution being unchanged after 10 days at room temperatures. Aqueous solutions of hydroxylamine deteriorate by the action of atmospheric oxygen and the autoxidation is markedly catalysable, e.g., by dissolved metals such as copper.[102, 103] Compounds such as potassium ethyl xanthate, 8-quinolinol, dithizone and polyethyleneamines, which are excellent complexants for Cu(I) and Cu(II), act as stabilizers. Hydroxylamine can be prepared as the free base, in high yields of pure material, by the ammonolysis of hydroxylammonium sulphate with liquid ammonia.[104] The formation of hydroxylamine in biological processes has been observed both from oxidation and from reduction methods. Thus the reduction of nitrates by micro-organisms yields hydroxylamine, and the origin and significance of the hydroxylamine have been discussed.[105] The seasonal variation of the hydroxylamine content in Lake Kizaki has been studied[106]; it is produced by the reduction of nitrates during the seasons when the waters are stagnant. The formation of hydroxylamine by reduction of nitrates by a micrococcus strain, M_{53}, isolated from dry sausages during ripening, was shown to be dependent on the pH of the media and the growth intensity of the culture.[107] The oxidation of ammonia to hydroxylamine by *Sterigmatocystis nigra* has been discussed as well as the possible analogous formation of protein amino-acids by reduction of α-keto acid oximes.[108–110] The reduction of nitrites by *Bacillus pumilus* produces hydroxylamine which however is attacked by another enzyme.[111]

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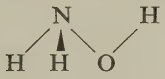
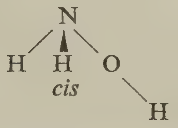
PHYSICAL PROPERTIES

The configuration of hydroxylamine has been variously described.[1] *X*-Ray measurements indicate that the molecule exists in the *trans* form in the solid state.[2]



trans



cis

A very comprehensive study of the infra-red spectrum of hydroxylamine has been made,[3] and the molecular structure related to the results. The values of certain thermodynamic functions were also derived from the results. Since pure hydroxylamine is so unstable, particular emphasis was laid on the measurements being accomplished with the pure material. The method of Lecher and Hofmann (Mellor, VIII, 284) was used to prepare pure hydroxylamine of melting-point 32–33°. Immediately prior to a spectrum being recorded the alcoholic solution was cooled to −15°, and the long crystals were filtered off and transferred to a desiccator flushed with dry nitrogen for twenty to thirty minutes. The pure compound was found to be quite stable when kept at 0° in an atmosphere of dry nitrogen, whereas it decomposed quite rapidly in air at room temperature. The spectrum of hydroxylamine vapour was recorded by introducing the sample into a side-tube fitted to a 1-m. absorption cell, and continuously evacuating the cell through a throttling valve. To prevent condensation the sample was kept at 45–50° and the cell about 10° higher. Owing to the extreme instability of the liquid it was not found possible to record a liquid-phase spectrum. A spectrum in the solid state was recorded by means of a Nujol mull in a low-temperature cell. The infra-red spectrum of hydroxylammonium chloride was obtained on a solid film produced by the evaporation of an alcoholic solution on a rock-salt plate. Table I gives the main bands and their assignments.

Table I.—Infra-Red Spectrum of Hydroxylammonium Chloride

Assignment	Vapour	Solid
NH_2 rock	765 (w) cm.$^{-1}$	845 (m) cm.$^{-1}$
NH_2 wag	1115 1125 } (v.s.)	1187 (v.s.)
OH bend	1357 (s)	1502 (m)
NH_2 bend	1605 (m)	1657 (m)
NH stretch	3297 (m)	3207 (s)
	3350 (w)?	3268 (s)
OH stretch	3656 (s)	3331 (s)
torsion	430 (v.w.)?	490 (v.w.)?

The spectrum of the hydroxylammonium ion is easily understood in relation to the spectrum of solid hydroxylamine, but there are two exceptional features. In general the stretching frequencies are decreased, and the blending frequencies are increased, except for the N–O stretching frequency. This exception is explained by the formal charge on the hydroxylammonium ion and not by the addition of a hydrogen atom to the nitrogen atom (cf. ref. 13). A second unusual feature is a strong peak at 1876 cm.$^{-1}$ for which there is no obvious explanation. The main features of the hydroxylammonium ion spectrum are given in Table II.

Table II.—Infra-Red Spectrum of the Hydroxylammonium Ion

Assignment	Frequency
N–O stretch	1000 cm.$^{-1}$
NH bend	1176 1200 } (s)
NH bend	1482 (s)
OH bend	1563 (s)
?	1876 (s)
NH stretch	2760 2795 } (w)
NH stretch	3025 (m)
OH stretch (?)	3080 (s)

The following molecular parameters best fit the observed frequencies: r_{N-O} 1·46 A., r_{O-H} 0·96 A., r_{N-H} 1·01 A., $\widehat{HON}$ 103°, $\widehat{HNO}$ 105°, $\widehat{HNH}$ 107°. Calculations of the rotational constants and moments of inertia show that the molecule is a very nearly symmetrical rotator, and indicate a trend for the *cis* configuration. However, detailed examination of the spectrum revealed satellite bands which are best explained on the basis that hydroxylamine, like nitrous acid and the alkyl nitrites, exists as a mixture of *cis* and *trans* forms. The moments of inertia, calculated for the *cis* form, were combined with the fundamental frequencies to calculate the thermodynamic properties of hydroxylamine in the ideal gaseous state from 300° to 1200°K. at 1 atmosphere. Some representative values are given in Table III.

The force constants of the various bonds were calculated to be: N–O, 3·89; O–H, 7·46; N–H, 6·11 × 10^5 dynes cm.$^{-1}$. It is this value for the force constant of the N–O bond which leads to the bond length of 1·46 A. An earlier[13] spectroscopic determination of this force constant, which gave the value 4·4 × 10^5 dynes cm.$^{-1}$, was criticized[3] on the ground that it was based on molecules which did not possess a normal covalent N–O single bond, namely, hydroxylammonium chloride, acetoxime, and trimethylamine-N-oxide. Other determinations gave the force constant as 3·97 × 10^5 dynes cm.$^{-1}$, in hydroxylamine,[14, 15] and 4·90 × 10^5 dynes cm.$^{-1}$ in its salts.[15–18]

The structures of the five methyl derivatives of hydroxylamine (*O*-methyl, *N*-methyl, *O,N*-dimethyl, *N,N*-dimethyl, and trimethylhydroxylamine) have been

Table III.—Thermodynamic Properties of Hydroxylamine

T (°K.)	$-(F^\circ-H_0^\circ)/T$	$(H^\circ-H_0^\circ)/T$	S°	C_p°	$(H^\circ-H_0^\circ)$ g.-cal. mole^{-1}
	g.-cal. deg.$^{-1}$ mole^{-1}				
298·16	47·36	8·98	56·33	11·17	2,677
300	47·42	9·00	56·39	11·20	2,700
400	50·10	9·76	59·88	13·02	3,904
600	54·36	11·34	65·70	15·74	6,804
800	57·82	12·67	70·49	17·39	10,136
1000	60·81	13·77	74·59	18·80	13,770
1200	63·45	14·69	78·17	19·82	17,628

investigated from their infra-red spectra.[4] The spectra were recorded from 4000 to 420 cm.$^{-1}$ on the vapour, liquid, and carbon tetrachloride solution. The nitrogen valencies were found to be pyramidally inclined and a skew or *trans* conformation about the N–O bond is preferred. In the *O*-methyl, *N*,*N*-dimethyl, and possibly the *N*-methyl derivatives the evidence suggests that two conformations exist in the vapour.

A study of the crystal structure of hydroxylamine, in which four molecules are in an orthorhombic unit cell, gave the N–O bond distance as $1{\cdot}47_6 \pm 0{\cdot}03$ A.[5] The closest intermolecular N····O distances were 2·74, 3·07, 3·11 and 3·18 A., which, assuming that the first two were involved in hydrogen bonds, leave the third hydrogen atom uninvolved and indicate a *trans*-configuration for the molecule. No residual entropy was indicated and no transition occurred when the hydroxylamine was cooled to −185°. It has been suggested that the hydrogen bond between the oxygen and nitrogen atoms in the hydroxylamine crystal structure is of the same type as that found in oximes, and that the observed 2·74 A. bond is O—H····N, while the observed 3·07 A. bond is O····H—N.[6] The bond of length 3·18 A. has been suggested as a third hydrogen bond involving the third hydrogen atom in a weaker interaction with a neighbouring oxygen atom.[7] Other structure determinations of hydroxylamine have been made.[8]

X-Ray study of the crystal structures of hydroxylammonium chloride and bromide gave the bonded N–O distance as 1·45 A.[9, 10] This is in good agreement with the calculated value of 1·435 A. for a covalent bond. The shortest distance between N and Cl^- at 3·16 to 3·25 A. is comparable with that in amine chlorides.

Infra-red measurements have been made on the hydrochlorides, hydrobromides and hydriodides of hydroxylamine and deuterohydroxylamine, at 25°, −78° and −180°.[11] Satisfactory vibrational assignments for NH_3O^- were made using, as basis, an ionic model in which one end (H_3NO) was axially symmetrical and the other end (OH) was of C_s type. The low values for NH and OH were attributed to weakening of the covalent hydrogen bonds and strengthening of electrovalent bonds by the distribution of the formal positive charge over all the atoms.

A theoretical study of the heights of asymmetric internal-rotation barriers about single bonds indicated that hydroxylamine should have a deep minimum in the *trans*-configuration and possibly a shallow minimum superimposed on the *cis*-maximum.[12]

Detailed results for the calculation of the atomic-core charge number and the estimation of bond polarities have been published for hydroxylamine.[19]

The positive shift of nuclear magnetic resonance of ^{14}N relative to the NO_2^- ion, normalized to 10,000 gauss, for hydroxylammonium chloride was found to be 5·20 gauss.[20] A proton magnetic resonance investigation of hydroxylammonium chloride has been made.[21]

As an extension of a study of the reaction between hydroxylamine and acetone, which indicated that the maximum rate of oxime formation occurred at pH 4·5, the dissociation constant of hydroxylamine was found to be $1{\cdot}07 \times 10^{-8}$ at 20°.[22] The pH values of 0·1 N., 0·05 N. and 0·025 N. solutions of hydroxylammonium chloride

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were found colorimetrically to be 3·5, 3·65 and 3·85 respectively; potentiometric methods were said to give unreliable results.[23] Using a glass electrode the hydrolysis constant, K_h, of hydroxylammonium chloride was $2{\cdot}5 \times 10^{-7}$ at 25°, which, using the equation:

$$\text{pH} = \tfrac{1}{2}\text{p}K_h - \tfrac{1}{2}\log\,[\text{NH}_4\text{O}^+]$$

gives the dissociation constant of hydroxylamine as 4×10^{-8}.[24] This very high figure was checked by the same method but with more refined materials and the relation[25]:

$$\text{pH} = \tfrac{1}{2}\text{p}K_h - \tfrac{1}{2}\log\,(Cf_{\text{H}+} - a_{\text{H}+})f_{\text{NH}_4\text{O}^+}$$

where C is the analytical concentration of hydroxylamine, a_{H^+} is the activity of the H^+ ion and f_{H^+}, $f_{\text{NH}_4\text{O}^+}$ are the activity coefficients of H^+ and NH_4O^+ ions respectively. K_h was found to be $1{\cdot}04 \times 10^{-6}$ at 25° and the dissociation constant to be $0{\cdot}97 \times 10^{-8}$. A value of $0{\cdot}87 \times 10^{-8}$ at 25° was obtained for the dissociation constant from a study of the distribution equilibrium of hydrochloric acid between ammonia and hydroxylamine.[25] A spectrophotometric determination of the dissociation constant at 30° gave $pK_B = 7{\cdot}675$ and $K_B = 2{\cdot}113 \times 10^{-8}$.[26] A conductometric determination of the hydrolytic constant gave $2{\cdot}202 \times 10^{-8}$ for the dissociation constant[27] at 30°.

From the values of the hydrolytic constant at 20° and 30°, use of the van't Hoff isochore gives the heat of hydrolysis as 2·37 kg.-cal. Solubility measurements give the values −4.13 kg.-cal. and + 1.96 kg.-cal. for the heats of solution and hydrolysis, respectively.[27]

During a study of the dependence of proton affinity on chemical constitution it was found that the hydroxyl group in hydroxylamine lowered the proton affinity relative to that of ammonia by 3·4 kg. cal. to 211 kg.-cal.[28]

The dielectric constants (ϵ) of aqueous solutions of hydroxylamine and of nitromethane have been measured and the dielectric coefficients ($d\epsilon/dc$) calculated (see Table IV).[28]

Table IV.—Dielectric Constants of Aqueous Solutions of Hydroxylamine and Nitromethane

Concentration (c)		Dielectric Constant (ϵ)	$d\epsilon/dc$
Hydroxylamine	0·000	77·85	
	0·225	77·64	−0·8
	0·27	77·63	
Nitromethane	0·000	77·85	
	0·132	77·62	−2
	0·199	77·41	
	0·285	77·29	

On the basis of these values the compromise structure, $\text{H}_3\text{N}^+\text{O}^-$, was suggested for hydroxylamine.

The mean heat capacity of hydroxylammonium chloride for the range 0° to 99·6° was found to be 0·3203 g.-cal. $\text{deg.}^{-1}\ \text{mole}^{-1}$.[30]

The molecular diamagnetism of hydroxylammonium chloride is $42{\cdot}45 \pm 0{\cdot}39 \times 10^{-6}$.[31] The difference of $6{\cdot}74 \times 10^{-6}$ between this value and that for ammonium chloride, $35{\cdot}71 \pm 0{\cdot}47 \times 10^{-6}$, agrees very closely with the predicted value.

Hydroxylamine displaces some absorbed dyes from a silver bromide surface and thus must become adsorbed in the ionized form by the surface.[32] Hydroxylamine produces the Sabattier effect when added to a developer bath but is less effective than many other substances,[33] e.g., hydrazine, which act as electron donors.

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The solubility of hydroxylammonium chloride in water has been studied up to 1000 atm. pressure.[34] Table V gives the freezing-points of aqueous solutions of hydroxylammonium chloride at atmospheric pressure.

Table V.—Freezing-Points of Aqueous Hydroxylammonium Chloride Solutions

Concentration (% of solution)	Freezing-pt. t°C.	Concentration (% of solution)	Freezing-pt. t°C.
1·072	−0·57	45·5	17
1·725	−0·93	48·55	25·1
5·099	−2·72	57·314	48·7
9·482	−5·33	58·983	55
15·431	−9·40	60·709	59
24·96	−17·10	62·074	60·6
29·38	−20·95	65·377	68
31·446	−22·92	74·224	89·6
32·957	−22·6	78·061	98·4
39·7	−0·9	100	150·5

The following equation was found to relate satisfactorily the solubility and temperature:

$$p = 40{\cdot}226 + 0{\cdot}30057t + 0{\cdot}001295t^2 - 0{\cdot}00000436t^3$$

where p is the solubility of the salt, g. per 100 g. of solution, at t°C.

The solubility measurements at elevated pressures gave rise to the solubility isobars and isotherms given in Tables VI and VII, respectively.

Table VI.—Temperatures (°C.) on Solubility Isobars of Hydroxylammonium Chloride in Water

% Concentration	Excess of Pressure, atmospheres				
	0	250	500	750	1000
45	15·28	16·14	17·14	18·38	19·77
50	29·43	30·34	31·51	32·88	34·53
55	42·81	43·81	45·08	46·64	48·46
60	55·57	56·65	58·06	59·78	61·84
65	67·83	68·99	70·53	72·44	74·72
70	79·73	81·01	82·68	84·76	87·27

Table VII.—Solubility in Water of Hydroxylammonium Chloride at High Pressures

Temperature °C.	Excess of Pressure, atmospheres				
	0	250	500	750	1000
20	46·64	46·335	45·98	45·55	45·08
40	53·93	53·56	53·11	52·56	51·95
60	61·76	61·31	60·74	60·06	59·28
80	70·11	69·57	68·87	68·03	67·06

From Table VII it can be seen that the solubility decreases with increasing pressure, which is in agreement with the Clausius–Clapeyron equation.

The density of hydroxylammonium chloride has been redetermined[34] as $d_4^{20} = 1{\cdot}680 \pm 0{\cdot}001$ and d_4^{20} $1{\cdot}676 \pm 0{\cdot}003$; it was found that the principal source of error was occlusion of air in the crystals. Schiff and Monsacchi (Mellor, VIII, 300) gave the following equation for the density of aqueous hydroxylammonium chloride:

$$d_4^{17} = 1 + 0{\cdot}00425\omega + 0{\cdot}0000095\omega^2$$

where ω denotes the percentage of salt in the solution, for values of ω from 3·5 to 40%. This equation has been verified for the values 9·48 and 24·96%[34]:

% Concentration	Density (obs.)	Density (calc.)
9·48	1·0410 ± 0·00015	1·0411
24·96	1·1117 ± 0·00015	1·1119

The adsorption of tracer quantities of radioactive zinc on an anion-exchange resin from solutions containing various chlorides depends on the nature of the cation.[35] An adsorption coefficient, D, was defined as:

$$D = \frac{(\text{Volume of solution in ml.}) \times (\text{Radioactivity in resin})}{(\text{Weight of resin in g.}) \times (\text{Radioactivity in solution})}$$

and graphs were plotted of log D against the total initial chloride concentration. In the majority of cases log D rises sharply and then either rises more slowly or falls steadily. In the case of hydroxylamine, however, after the initial rise log D is almost constant. This observation is due possibly to the strong tendency which zinc has of forming complexes with hydroxylamine (see page 135).

The absorption spectrum of $(NH_3OH)Cr(SO_4)_2,12H_2O$ at 20°K. in the range 14,400 to 16,300 cm.$^{-1}$ has been examined and the frequencies, intensities and line widths for 64 lines tabulated.[36] The vapour pressures of alums containing hydroxylamine were found to be higher than expected from the ionic radii, and were ascribed to the non-noble gas character of the ion.[37] The heat of hydration and mean aqueous vapour pressure of $(NH_3OH)Al(SO_4)_2,12H_2O$ have been investigated and the values of the constants, A and B, in the equation:

$$\log p = B + (A/T)$$

calculated.[38] The magnetic susceptibilities of the Cr^{3+} alums represented by the formula, $CrA(XY_4)_2,12H_2O$, where A is K, Rb, Cs, NH_4, Tl, or NH_2OH, and $(XY_4)_2$ is $(SO_4)_2$, $(SeO_4)_2$, or $(SO_4)(SeO_4)$, have been measured over the range 300° to 100°K.[39] The hydroxylamine chrome alum, $Cr_2(SO_4)_4,(NH_3OH)_2SO_4,24H_2O$, was unusual in that the splitting factor had a lower value in the low-temperature range, whereas in all the other cases this value was appreciably higher than in the high-temperature range. This anomaly was ascribed to the splitting factor varying with temperature in such a way as to mask the positive value of the high-frequency term. The variation of the square of the mean effective magnetic moment, ρ_f^2, with temperature is illustrated in Table VIII.

Table VIII.—Mean Effective Magnetic Moments of $Cr_2(SO_4)_3,(NH_3OH)_2SO_4,24H_2O$

Temperature	ρ_f^2, Bohr magnetons		Temperature	ρ_f^2, Bohr magnetons	
°K.	obs.	calc.	°K.	obs.	calc.
300	14·68	14·68	180	14·71	14·80
280	14·69		160	14·80	14·79
260	14·68		140	14·86	14·87
240	14·67		120	14·85	14·86
220	14·66		100	14·80	14·81
200	14·68				

A solution of hexahydroxylamidocobalt(III) perchlorate in 0·1 N. perchloric acid absorbs at much higher frequencies than other hexa-amine complexes[40] (see Table IX).

Table IX.—Absorption Data for Cobalt Complexes

Complex ion	p*K* of co-ordinating amine	Frequency in 10^{13} sec.$^{-1}$ units	
		1st Band	2nd Band
$[Co(NH_2OH)_6]^{3+}$	6·03*	68·5 (log ϵ=2·07)	*ca* 94 (log ϵ=2·3)
$[Co\ en_3]^{3+}$	8·55	63·9	88·4
$[Co(NH_3)_6]^{3+}$	9·27	62·9	88·3
$[Co(NH_3)_4(CH_3NH_2)_2]^{3+}$	10·63	61·9	86·3

* Ref. 25

The much higher values for the hydroxylamine complex may indicate strong interaction between the central cobalt(III) atom and the nitrogen atoms of the co-ordinating molecules.

The complexes formed between ferric ions and simple hydroxamic acids, hydroxylamine, siderophyllin and conalbumin have similar absorption maxima at 460–465 mμ; the presence of carbon dioxide was found to be necessary for the formation of the complexes from the last three compounds.[41]

The *X*-ray spectrum discontinuities of the platinum complexes $Pt(NH_2OH)_4(OH)_2$ and $Pt(OH)_2(NH_2OH)_2$ have been examined.[42]

The presence of a low concentration of hydroxylammonium sulphate raised the oxygen overpotential at a platinum electrode by 0·22 v. The effect, which was specific for platinum, appeared to be due to the removal of some intermediate essential to the evolution of oxygen.[43]

The half-wave potential of hydroxylamine, at constant ionic strength, increased by 90 mv./pH from −0·430 v. at pH 13 to +0·037 v. in a neutral buffer. The oxidation was described by the equation[44]:

$$2NH_2OH + 6OH^- \rightleftharpoons N_2O_2^{--} + 6H_2O + 4e^-$$

The oxidation of hydroxylamine was studied with gold, graphite and platinum electrodes and qualitative studies indicated reasonable agreement between half-wave potentials and critical oxidation potentials. Quantitative studies indicated fair reproducibility but the relation between diffusion current and concentration was non-linear.[45]

The polarographic reduction of hydroxylammonium chloride on a mercury-drop electrode has been accomplished in the presence of ions of differing valencies.[46] In particular the system NH_2OH,HCl was investigated.[46, 47] The curve was characterized by two waves, the second of which increased as the concentration of the hydroxylamine was increased. The phenomenon was explained by the following equations[48]:

$$NH_3OH^+ + 2e^- + 2H^+ \rightarrow NH_4^+ + H_2O$$
$$NH_2OH + 2e^- + 3H^+ \rightarrow NH_4^+ + H_2O$$

The first equation accounts for the first wave in unbuffered solutions and takes place at more positive potentials. The second wave is held to correspond with the reduction represented by the second equation. Equations are given which give good agreement between the calculated and experimental values of the current strength.

The catalytic reduction of hydroxylamine was held responsible for the production of a kinetic current in the polarography of the iron(III)-triethanolamine complex in the presence of hydroxylamine.[49] The Fe^{2+} complex, formed at the cathode, was oxidized by the hydroxylamine and the free radical so produced reacted with another molecule of the Fe^{2+} complex. In strong alkali the decrease of the rate constants was attributed to the acidic dissociation of hydroxylamine, the dissociation constant approaching 10^{-14} at an ionic strength of 0·72.

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REACTIONS AND CHEMICAL PROPERTIES OF HYDROXYLAMINE AND ITS SALTS

The inorganic reactions of hydroxylamine in solution can be conveniently divided into (*a*) those which make use of its reducing power, (*b*) a few in which it is itself reduced, (*c*) complex-forming reactions and (*d*) others.

Hydroxylamine as Reducing Agent

The behaviour of hydrogen peroxide, hydroxylamine and hydrazine as reducing agents in acidic solutions and as oxidizing agents (to a certain extent) in neutral or

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alkaline media has been discussed in the light of the Brønsted theory.[1] It is thought that the reactions of hydroxylamine can be directly related to those of the NH_2 radical, which can act both as an oxidizing and reducing agent.[2] On this basis the reactions of hydroxylamine leading to nitrogen, nitrous oxide, hydrogen azide and ammonia were developed in detail, and the following equation for the reaction of iodine with hydroxylamine was proposed:

$$2NH_2OH.H^+ + 2I_2 \rightarrow N_2O + 4I^- + 6H^+ + H_2O$$

This reaction had been studied previously and conflicting reports on the influence of light have appeared. Thus, it was assumed[3, 4] that the reaction is bimolecular in the dark with a temperature coefficient of 2·54 (20–30°), and with decreasing wavelength the temperature coefficient decreases to, for example, 2·28 at 8500 A., 2·25 at 7304 A., 2·1 at 5650 A. and 1·94 at 4725 A. However, later workers reported a temperature coefficient of 4·0 over the same temperature range and the reaction appears to be less sensitive to light than was previously claimed.[5] The active oxidizing agent was assumed to be HIO. The total absorption of light from a copper arc by hydroxylammonium chloride and iodine is greater than the sum of the separate absorptions and varies with the concentration of the former.[6] The reaction in sunlight between hydroxylammonium chloride and iodine is sensitized by zinc chloride.[7] More recent studies indicate that the amount of iodine reduced increases with dilution (using up to 100% excess of iodine) and with increased temperature.[8, 9] The reaction proposed is:

$$NH_2OH + 2I_2 + H_2O \rightarrow HNO_2 + 4HI$$

However, in the presence of sulphuric acid, acetic acid or sodium sulphate, the amount of iodine absorbed is less than that indicated by the above equation. This is probably because the iodine is liberated more rapidly than it is absorbed, after the maximum is reached. Similar results are obtained with chloride and nitrate ions and with potassium salts. The induction by Ti^{3+} of the oxidation of iodide to iodine by hydroxylamine has also been discussed[10]; Ti^{4+} is simultaneously formed. The reaction between silver bromide and hydroxylamine gives nitrogen and nitrous oxide. In the presence of sodium hydroxide the following reactions are proposed[11]:

$$2NH_2OH + 2AgBr \rightarrow 2Ag + N_2 + 2HBr + 2H_2O$$
$$2NH_2OH + 4AgBr \rightarrow 4Ag + N_2O + 4HBr + H_2O$$

With ammoniacal silver nitrate nitrogen only is evolved. The reaction between silver ion and hydroxylamine is catalysed by colloidal gold or silver and the rate of nitrogen evolution equals the rate of silver formation.[12] The NH_2O^- ion is considered to be the active reducing agent. In a study of the surface conditions of silver salts, it was found that at pH 10·2–10·8 nitrogen only is evolved.[13] A later investigation by the same worker included silver chloride, silver cyanide, mercurous chloride and cupric hydroxide.[14] The conclusion reached is that two reactions can occur between silver salts and hydroxylamine: (i) the silver-catalysed oxidation yields nitrogen as the almost exclusive gaseous product; (ii) an uncatalysed oxidation leads to the formation of nitrous oxide. The yield of nitrous oxide increases on ageing of the silver salt, which is taken to indicate perfection of the lattice. In the use of an actual photographic emulsion the results were similar to those found with pure silver chloride and silver bromide; the catalytic mechanism is applicable and fog formation is ascribed to an uncatalysed reaction.[15] Mercurous chloride reacted in the same way as the silver salts.[14, 16] Mercurous nitrate oxidizes hydroxylamine, with an induction period, to give mainly nitrous oxide; in the presence of colloidal mercury or silver catalysts the main product is nitrogen.[17] The two-stage reaction of mercuric oxide with hydroxylamine can be demonstrated by performing the reaction in the capillaries of filter paper.[18] Blue cupric hydroxide reacts rapidly at pH 10·2 to give nitrous oxide almost exclusively.[14] The initial reaction rate decreases as the precipitate ages and the formation of cupric oxide is indicated by a sharp break in the reaction curve; when this occurs nitrogen is also formed and the amount produced is a measure of the amount of conversion of cupric hydroxide into cupric oxide. The reduction of cupric ion to cuprous ion and metallic copper by varying concentrations of hydroxylamine in silica gels has been used in a study of their structure[19]; using a 1% solution, but not 2%, the reduction products appear as Liesegang rings. In a study of the radical, NOH, this entity was produced by the oxidation of hydroxylammonium chloride by cupric ion and was assumed to be co-ordinately linked to cuprous ion.[20] The reduction of cupric ion by hydroxylammonium chloride has been used as the basis of a colour reaction for acetylene.[21] Cupric sulphate pentahydrate is reduced by hydroxylammonium chloride in the presence of ammonia at pH 5·3 (adjusted with sulphuric acid); the solution, which is stable, unlike the Ilosvay reagent, gives with acetylene a blue colour which can be used for both the determination and detection of acetylene. The complex from cupric sulphate and hydroxylamine has been investigated as a proöxidant system in the autoxidation of fats and oils; its action is less than that of the complex formed from cupric sulphate and colamine.[22] The reduction of cupric ion by hydroxylamine is said to be bimolecular, each gram-atom of cupric ion requiring two moles of hydroxylamine; the mechanism of the reaction in the presence or absence of proteins was also discussed.[23] When colloidal gold was added to a mixture of gold chloride and hydroxylammonium chloride, the particle size was increased.[24]

The course of the reaction between potassium permanganate and hydroxylamine in varying concentrations is explained by assuming that two simultaneous reactions take place, namely the normal one and an autocatalytic one.[25] The actual catalyst in acidic solution is assumed to be Mn(III, IV or V) formed from Mn^{++} and MnO_4^-. The reduction of 0·05 M. sodium dichromate, acidified with perchloric acid, by hydroxylamine gives a solution, the visible and ultra-violet spectra of which are identical with those of Cr(III) in solutions of chromium(III) perchlorate.[26] The preparation of hydrophobic selenium colloidal solutions by the reduction of selenium dioxide by hydroxylamine has been improved.[27] Hydroxylamine has been used to prepare polonium metal by the reduction of polonium hydroxide.[28]

Oxidation of hydroxylamine at a dropping mercury electrode proceeds as follows:

$$2NH_2OH + 6OH^- \rightleftharpoons N_2O_2^{2-} + 6H_2O + 4e$$

which is in accord with the electrochemical data.[29]

Mass-spectrographic analysis shows that appreciable amounts of nitrous oxide are produced during the oxidation of hydroxylamine by hypochlorite.[30]

Hydroxylamine as Oxidizing Agent

Hydroxylamine is reduced to ammonia by alkaline stannite solutions[31] and by alkaline arsenite solutions.[32] It was also found that, when distilled in the presence of alkali alone, hydroxylamine gives ammonia according to the equation:

$$3NH_2OH = NH_3 + 3H_2O + N_2$$

and an earlier suggestion by A. Michael (1921) that explosive sodium hydroxylamate exists appears unlikely. In the presence of arsenite the most probable reaction is:

$$2OH^- + AsO_2^- + NH_2OH \rightleftharpoons AsO_4^{---} + NH_3 + H_2O$$

If a small quantity of tin(IV) chloride is added to a solution of hydroxylammonium chloride in hydrochloric acid no reduction is observed and the potential of the solution is equal to that of a solution of tin(II); if now a small quantity of a solution containing perrhenic ion is added the reduction proceeds.[33] During the reduction the potential of the solution is 0·65 v.; when two equivalents of the reducing agent have been added the potential drops sharply, indicating that the reduction is complete:

$$NH_3OH^+ + 2H^+ + 2e \rightarrow NH_4^+ + H_2O$$

The calculated potential for this reaction is 1·35 v., but this value is not achieved in the above conditions. The potentials referred to are the normal potentials at 25° on the hydrogen scale. The observed value is very close to that found for a solution of perrhenic acid at a similar dilution in the presence of a trace of tin(II) chloride. In the presence of the catalyst and with one-third excess of reducing agent, hydroxylamine is quantitatively reduced during ten minutes. The calculated potential for the system N_2O/NH_3OH^+ is $-0{\cdot}05$ v. but in conditions similar to the above an apparent potential of 0·70 to 0·75 v. is observed for the oxidation of hydroxylamine by nitrous acid. In this case hydroxylamine is a less powerful reducing agent than is indicated by the calculated figure.

Iron reduces hydroxylamine in the presence of aqueous solutions of neutral salts.[34]

Reduction of hydroxylamine and of hydroxylammonium ions to ammonium ions at the dropping mercury cathode has been investigated under various conditions, notably those involving different valencies of other ions present in the solution.[35–37] Catalytic reduction of hydroxylamine by the ferric–triethanolamine complex is invoked to account for a kinetic current observed in the polarography of the complex in the presence of hydroxylamine.[38]

In the reduction of the oxalate complex of Ti(IV) in oxalic acid at a dropping mercury cathode, in the presence of hydroxylamine, it was found that a kinetic current was produced.[39] This current was proportional to the concentration of hydroxylamine and was produced by the electro-reduction of Ti(IV) to Ti(III) followed by chemical oxidation of the latter back to the former, by the hydroxylamine, thus:

$$Ti^{3+} + NH_3OH^+ \rightarrow Ti^{4+} + H_2O + NH_2$$

The NH_2 radical reacted with the excess of oxalic acid. The results obtained from the catalytic reduction of Ti(IV) in the presence of hydroxylamine were shown to agree with the conclusions drawn from a theoretical treatment of electron-transfer processes followed by chemical reaction, in voltammetry at constant current.[40]

The catalytic hydrogenation of hydroxylamine in the presence of active platinum yields ammonia and nitrous oxide.[41]

The reduction of hydroxylamine has been studied in polymerization systems. When hydroxylamine is decomposed on colloidal metals it is unable to initiate polymerization.[42] Emulsion copolymerization of butadiene and styrene is virtually prevented by hydroxylammonium chloride.[43] The rapid polymerization of vinyl monomers at low temperatures, e.g. $-25°$, in aqueous systems, is however brought about by the use of VSO_4 or Ti^{3+} as the initiator and hydroxylammonium chloride as the oxidizing agent.[44, 45] From a kinetic study of the reduction of hydroxylammonium chloride in acidic solution by some metals in their lower valency states, in the presence of methyl methacrylate, benzene etc. the following reaction appears to be the first step in a two-step process[46]:

$$M^{n+} + HONH_3^+ \rightarrow M^{(n+1)+} + NH_2 + (OH^- + H^+)$$

The NH_2 radical thus formed effectively initiates the polymerization of the methyl methacrylate. In the case of benzene, biphenyl is one product formed. The alternative mechanism:

$$M^{n+} + HONH_3^+ \rightarrow M^{(n+1)+} + OH + (H^+ + NH_2^-)$$

is 12·5 kcal. less exothermic than the one proposed. The most effective reducing agent is Ti(III), while reduction by Cr(II), V(II), Mo(III), and Fe(II) proceeds at lower rates.

In an investigation of the ultra-violet photoreduction of dilute nitrate solution:

$$HNO_3 \rightarrow HNO_2 \rightarrow H_2N_2O_2 \rightarrow NH_2OH \rightarrow NH_4OH$$

it was found that catalytic disproportionation of hydroxylamine occurs in the presence of glucose, methanol, formic acid or ascorbic acid[47]:

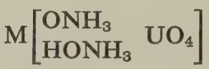
$$NH_2OH \rightarrow NH_3 \text{ and } N_2O$$
$$NH_2OH + NO_2^- \rightarrow N_2 + N_2O$$

Formation of Complexes

The precipitates formed by hydroxylamine with aluminium, chromium, iron, cobalt, nickel, zinc, and cadmium have been likened to those formed by ammonium hydroxide.[66] Colloidal $Cu_2Fe(CN)_6$ gives, with hydroxylamine, a compound which fluoresces green in subdued light and blue in sunlight.[66, 67]

Among several complex sulphates of gallium and various bases, the hydroxylamine derivative, $(NH_2OH)_2,H_2SO_4,Ga_2(SO_4)_3,24H_2O$, has been described; it is efflorescent and insoluble in ethanol.[79]

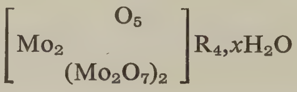
In the pH range 6–8 hydroxylamine and uranyl nitrate react to give the complex $(NH_3OH)_2UO_4,H_2O$; at pH values greater than 8 soluble complexes are formed of the type[80]:



$$M\left[\begin{array}{ll}ONH_3 & \\ HONH_3 & UO_4\end{array}\right]$$

where M is an alkali metal.

The complexes between hydroxylamine and molybdenum (Mellor, VIII, 293) have been re-examined. Two different accounts of the structures and valency states of the molybdenum have been given. In the first,[77] the red substance obtained by heating together a molybdate and an excess of hydroxylamine is assigned the formula $Mo_2O_5,4MoO_3,2R_2O,xH_2O$ ($R = NH_4$, K, or Na) with the structure of a "molybdicopentaoxomolybdate":



$$\left[\begin{array}{ll} & O_5 \\ Mo_2 & \\ & (Mo_2O_7)_2\end{array}\right]R_4,xH_2O$$

The other view[78] is that the compounds contain hexavalent molybdenum only and have the structure:

$$\left[[Mo_2NOH](MoO_4)_9\right]\begin{array}{l}M_4\\H_4\end{array}$$

It is held that the initial stage in the reduction produces a complex of molybdenum (VI) and $2NOH^{--}$ ions but that an internal deformation of electronic orbits within the complex completes the reduction and that the molybdenum(VI) is transformed into molybdenum(IV) and the NOH^{--} into NOH^-.

Other molybdenum compounds with hydroxylamine can be prepared by varying the reaction conditions. Prolonged heating converts the complexes into "molybdicomolybdates" of the general formula[77]: $Mo_2O_5,4MoO_3,2R_2O,8H_2O$.

Hexahydroxylamidocobalt(III) chloride is conveniently prepared as follows: a concentrated aqueous solution of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride, $[Co\ en_2\ Cl_2]Cl$, and hydroxylammonium chloride is treated, below 0°, with concentrated aqueous sodium hydroxide and the mixture vigorously stirred. After the appearance of a light brown precipitate a large excess of concentrated hydrochloric acid is added, whereupon the solution turns dark green and within a few minutes the desired complex separates as glittering golden leaflets. After one hour the product is filtered off, dissolved in slightly acidic warm water and reprecipitated by the addition of concentrated hydrochloric acid. The corresponding bromide and perchlorate can be prepared by the addition of the appropriate concentrated acid to a concentrated solution of the chloride. When kept the chloride and bromide change into the cobalt(II) complex even in a closed vessel; the perchlorate however is quite stable, even in warm weather and in sunlight, in the absence of moisture. The complexes decompose rapidly when dissolved in water; this decomposition is prevented by the addition of the corresponding strong acid. The decomposition of the cobalt(III) complex to a cobalt(II) species was studied over the range pH 4·8–5·8 at 25–50°, and was found to be second-order with respect to hydroxyl ion and cobalt(III) complex. The following equation was proposed:

$$[Co(NH_2OH)_6]^{3+} + H_2O \rightleftharpoons [Co(NH_2OH)_5(NHOH)]^{2+} + H_3O^+$$

The activation energy is 32·5 kcal./mole.

Whereas complexes of cobalt(III) with ammonia, ethylenediamine, 1,2-diaminopropane, and diethylenetriamine, when caused to react with silver oxide, give the complex hydroxide, the corresponding hydroxylamine compound must be prepared from the chloride and calcium hydroxide.[75]

The action of hydroxylamine on nickel cyanide or $K_2Ni(CN)_4$ gives a violet complex containing the ion, $Ni(CN)_3$, the formula $H_2O,(CN)_2Ni{-}N(OH){-}Ni(CN)_2,H_2O$ being proposed for the product from nickel cyanide.[68] Later work,[69] in which $K_2Ni(CN)_4,2H_2O$ was heated with hydroxylammonium chloride and 40% aq. potassium hydroxide until the evolution of ammonia ceased, gave the structure of the stable violet complex as $K_2[Ni(CN)_3n,N(OH){-}Ni(CN)_3]$; it can also be prepared by the action of hydrazine hydrate on nickel cyanide in aqueous potassium hydroxide. The formation of NO-type complexes has been explained by the preliminary formation of dihydroxyammonia, thus[70, 71]

$$2NH_2OH \rightarrow NH_3 + NH(OH)_2$$

$$NH(OH)_2 \rightarrow HNO + H_2O$$

$$HNO + OH^- \rightarrow NO^- + H_2O$$

$$Ni(CN)_4^{--} + NO^- \rightarrow [Ni(CN)_3NO]^{--} + CN^-$$

The driving force is the transformation of NO^- to NO^+ in the complex, together with the formation of the rare-gas structure (eighteen electrons in the 3*d*, 4*sp* levels of the ground state) in the tetrahedral NO-complex, from the planar tetracyano anion (sixteen electrons in the 3*d*–4*sp* level). The violet substance was also obtained from $K_2[Ni(CN)_3]$ and nitric oxide and shown, spectroscopically, to be identical with that from $K_2[Ni(CN)_4]$ and hydroxylamine, the structure $K_2[Ni(CN)_3NO]$ being proposed.

The formation of the short-lived NOH during the hydrolysis of hydroxylamido-*O*-sulphates, -*N*-sulphates, and -*N*,*O*-disulphates, was demonstrated by the formation of the violet complex $K_2[Ni(CN)_3NO]$, which was shown to be a very sensitive test.[72]

The reaction of hydroxylamine with nickel iodide gives a red substance assumed to be $[Ni(NH_2OH)_6]I_2$.[73] In the same work a bluish compound was made from hydroxylamine and nickel chloride; in the product the ratio Ni:Cl:NH_2OH was 2:3:5, and, by the slow evaporation of an aqueous solution of hydroxylamine and nickel chloride over anhydrous calcium chloride, the compound $Ni(NH_2OH)_4Cl_2$ was obtained as intensely blue monoclinic crystals. By double decomposition with sodium hexanitrocobaltate(III), $Na_3[Co(NO_2)_6]$, this blue compound gave $Na_4[Ni(NO_2)_6]$.

In a study of diamagnetic nickel derivatives, the compound $Ni(NH_2OH)_6SO_4$ was prepared and shown to have μ_{eff} approx. 2·9 magnetons, which is approximately that of the usual nickel complex.[74]

The formation and reactions of complex compounds of hydroxylamine and platinum and palladium have been extensively studied. The compounds from Pt(II) and from Pt(IV) are very numerous and range from the easily prepared salts of the Magnus type, e.g., $[Pt(NH_2OH)_4]PtCl_4$, to the less readily accessible mixed tetrammines such as $[Pt(II)(NH_2OH)(NH_3)(C_5H_5N)(C_5H_4N.\alpha NH_2)]Cl_2$. The hydroxylamine is a primary target for oxidation and yields an unstable intermediate grouping of the type $(NH_2OH)Cl_2$.[49, 50] This group has a strong labilizing effect on groups in the *trans* position to it, and thus renders them easily replaceable. E.g., when $[Pt(NH_2OH)_4](OH)_2$ is treated with chlorine, after the initial attack, further hydroxylamine groups are quickly replaced giving rise to a precipitate of $[Pt(NH_2OH)_4]PtCl_4$. Further chlorination leads to H_2PtCl_6, which is also formed directly from $[Pt(NH_2OH)_4]Cl_2$ and chlorine. The *trans* effect of the postulated intermediate group was demonstrated with other compounds such as *cis* $[Pt(NH_2OH)_2(NH_3)_2]Cl_2$ which yields H_2PtCl_6 and the *trans* isomer, which gives $Pt(NH_3)_2Cl_4$. In the *cis* isomer the ammonia and hydroxylamine groups are *trans* with respect to each other, whereas in the *trans* isomer this is not the case. The oxidation of mixed Pt(II) tetrammines with concentrated hydrobromic acid has been

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shown to lead to Pt(IV)–NH_2OH complexes, which react with Pt(II) compounds giving compounds of the general formula $[PtAA'Br_2][PtAA'Br_4]$. A and A' may be the same or different; e.g.,

$$cis[Pt(NH_2OH)_2(NH_3)_2]Cl_2 \xrightarrow{HBr} [Pt(NH_2OH)(NH_3)Br_2][Pt(NH_2OH)(NH_3)Br_4]$$

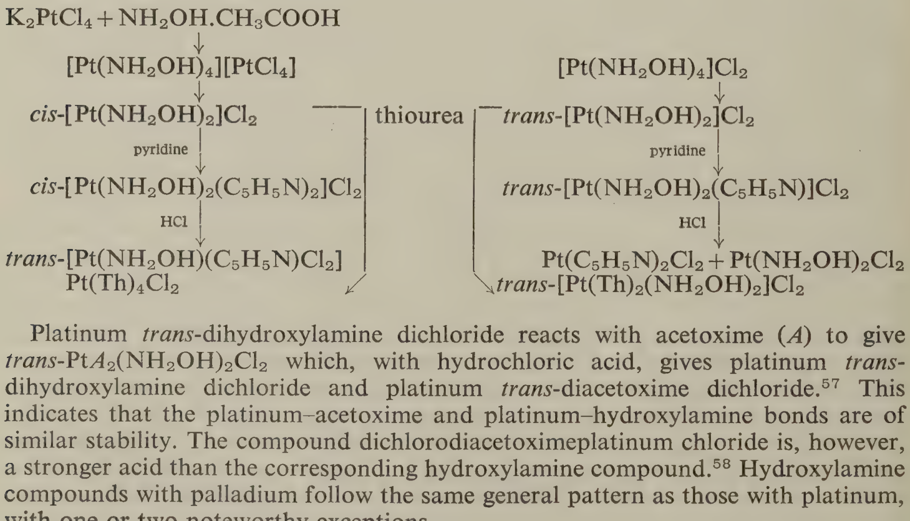
The action of hydrobromic acid on *cis*.-$[Pt(NH_2OH)_4]Cl_2$, $[Pt(NH_2OH)_2(NH_3)_2]Cl_2$ and $[Pt(NH_2OH)_2(C_5H_5N)_2]Cl_2$ gives *trans*-$[Pt(NH_2OH)_2Br_4]$, $[Pt(NH_2OH)(NH_3)Br_4]$ and $[Pt(NH_2OH)(C_5H_5N)Br_4]$ respectively.[52] It was postulated[52, 53] that the oxidant is the liberated hydroxylamine, acting in its tautomeric form NH_3O. Iodides of Pt(II) diamines can be prepared from the corresponding chlorides and potassium iodide.[50] These react with other amines to form triammines $[PtAA'A_2'']I_2$, where A'' is the entering amine, and A,A',A'' can be the same or different. The bases used were hydroxylamine, ammonia, pyridine, α-aminopyridine and thiourea. Bromides can be prepared in the same way or by the action of hydrobromic acid on tetrammines,[53] e.g.,

$$[PtA_2A_2']Cl_2 + 2HBr \rightarrow [PtAA']Br_2 + A.HCl + A'.HCl$$

The tetrammine having four different co-ordinating groups, namely $[Pt(NH_2OH)(NH_3)(C_5H_5N)(C_5H_4N.\alpha NH_2)]Cl_2$, was prepared[54] by stepwise substitution from the chloroplatinate via Peyrone's salt, followed by the reactions:

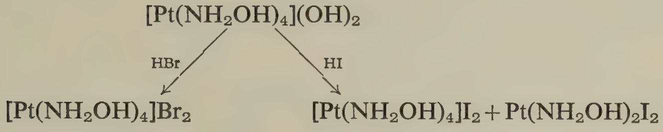
$$\rightarrow cis\text{-}[Pt(NH_2OH)_2(NH_3)_2]Cl_2 \rightarrow trans\text{-}[Pt(NH_2OH)(NH_3)Cl_2]$$
$$\rightarrow trans\text{-}[Pt(NH_2OH)(NH_3)(C_5H_5N)Cl]Cl \xrightarrow{\alpha\text{-}NH_2\cdot C_5H_4N} \text{tetrammine}$$

Attempts to use aliphatic amines in place of the α-aminopyridine led only to resinous products. The successful preparation of $[Pt(NH_2OH)_2Cl_2]$ from K_2PtCl_4 and hydroxylamine was carried out under mild conditions, heating and dilution being avoided.[55, 56] The use of hydroxylammonium acetate prevented the introduction of more than two molecules of hydroxylamine. The *cis* configuration of the product was established by means of Kursanov's reactions, whereby the action of thiourea (Th) led to yellow $PtTh_4Cl_2$, whereas the *trans* compound, previously prepared by the reactions: $[Pt(NH_2OH)_4]Cl_2 + 2HCl \rightarrow Pt(NH_2OH)_2Cl_2 + 2NH_3OHCl$, gives white $[Pt(NH_2OH)_2(Th)_2]Cl_2$. Confirmation was provided by Jorgensen's reaction with pyridine, followed by hydrochloric acid giving *trans*-$[Pt(C_5H_5N)(NH_2OH)Cl_2]$, via *cis*-$[Pt(NH_2OH)_2(C_5H_5N)_2Cl_2]$; where the *trans* compound is known to give *trans*-$Pt(C_5H_5N)_2Cl_2$ and $Pt(NH_2OH)_2Cl_2$:

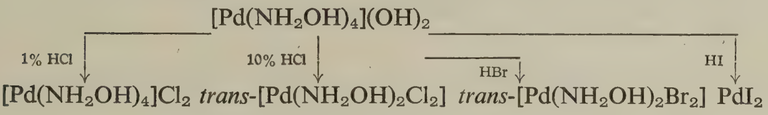

$K_2PtCl_4 + NH_2OH.CH_3COOH$
$[Pt(NH_2OH)_4][PtCl_4]$
$[Pt(NH_2OH)_4]Cl_2$
cis-$[Pt(NH_2OH)_2]Cl_2$
thiourea
trans-$[Pt(NH_2OH)_2]Cl_2$
pyridine
pyridine
cis-$[Pt(NH_2OH)_2(C_5H_5N)_2]Cl_2$
trans-$[Pt(NH_2OH)_2(C_5H_5N)]Cl_2$
HCl
HCl
trans-$[Pt(NH_2OH)(C_5H_5N)Cl_2]$
$Pt(C_5H_5N)_2Cl_2 + Pt(NH_2OH)_2Cl_2$
$Pt(Th)_4Cl_2$
trans-$[Pt(Th)_2(NH_2OH)_2]Cl_2$

Platinum *trans*-dihydroxylamine dichloride reacts with acetoxime (A) to give *trans*-$PtA_2(NH_2OH)_2Cl_2$ which, with hydrochloric acid, gives platinum *trans*-dihydroxylamine dichloride and platinum *trans*-diacetoxime dichloride.[57] This indicates that the platinum–acetoxime and platinum–hydroxylamine bonds are of similar stability. The compound dichlorodiacetoximeplatinum chloride is, however, a stronger acid than the corresponding hydroxylamine compound.[58] Hydroxylamine compounds with palladium follow the same general pattern as those with platinum, with one or two noteworthy exceptions.

Hydroxylamine and K_2PdCl_4 form the base $[Pd(NH_2OH)_4](OH)_2$ and experiments show that the palladium–hydroxylamine bond is weaker than the platinum–hydroxylamine bond in corresponding compounds.[59, 60] Mixed compounds containing both platinum and palladium are easily prepared,[59, 61] e.g., $[Pd(NH_2OH)_4][PtCl_4]$, $[Pd(NH_2OH)_2(NH_3)_2][PtCl_4]$, $[Pt(NH_2OH)_4][PdCl_4]$, $[Pt(NH_2OH)(C_5H_5N)(NH_3)_2][PdCl_4]$, $[Pt(NH_2OH)_2(NH_3)(C_5H_5N)][PdCl_4]$. Platinum dihydroxylamine dihydroxide reacts with H_2F_2 to form $[Pt(NH_2OH)_4](HF_2)_2,2H_2O$ and the corresponding palladium compound $[Pd(NH_2OH)_4](HF_2)_2,2H_2O$ is formed similarly.[60, 62] However, the reactions with hydrochloric, hydrobromic and hydriodic acids follow a different course. Thus:

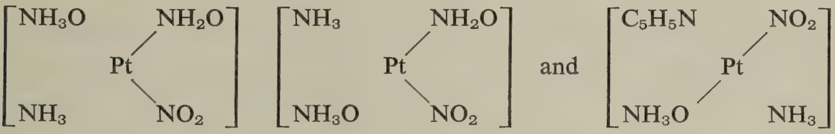


$$\begin{tikzcd} & {[Pt(NH_2OH)_4](OH)_2} \arrow[dl, "HBr"'] \arrow[dr, "HI"] & \\ {[Pt(NH_2OH)_4]Br_2} & & {[Pt(NH_2OH)_4]I_2 + Pt(NH_2OH)_2I_2} \end{tikzcd}$$



$$\begin{tikzcd} & & {[Pd(NH_2OH)_4](OH)_2} \arrow[dll, "1\%\ HCl"'] \arrow[dl, "10\%\ HCl"] \arrow[d, "HBr"] \arrow[dr, "HI"] & \\ {[Pd(NH_2OH)_4]Cl_2} & trans\text{-}[Pd(NH_2OH)_2Cl_2] & trans\text{-}[Pd(NH_2OH)_2Br_2] & PdI_2 \end{tikzcd}$$

Earlier work gave *trans*-$[Pt(NH_2OH)_2Br_2]$ and $(NH_2OH)_2PtBr_5$ as the products of the reactions between $[Pt(NH_2OH)_4](OH)_2$ and 10% and boiling concentrated hydrobromic acid respectively. In the same work are described the preparation and transformations of several platinum complexes with hydroxylamine, e.g., *cis*- and *trans*-$[Pt(NH_2OH)_2(NO_2)_2]$, $[Pt(C_2O_4)(NH_2OH)_2]$, $[Pt(NH_2OH)_4][Pt(C_2O_4)_2]$, $[Pt(NH_2OH)_2(NO_2)(NH_3)]Cl$ and many others. The compounds formulated



are given as examples of the increase in acidic properties of hydroxylamine due to the proximity of the nitro group, the effect being compared with the enhancement of the activity of the –OH group in picric acid.

In a study of the directing influence of the nitro-group in palladium(II) complexes, the preparation of dichlorodihydroxylamido platinum, by Goremykin's method,[62] is described.[64] When this compound is caused to react with sodium nitrite, reduction occurs at each of the temperatures used, viz. 10–12°, 25–30° and 35–40°; a constant analysis for $Pd(NH_2OH)_2(NO_2)_2$ was not obtained.

trans-Dihydroxylamidodi-iodoplatinum, $Pt(NH_2OH)_2I_2$, forms nearly square dark-orange platelets, 1 mm. wide and 0·1 mm. thick, as monoclinic holohedra, C_{2h}–$2m$, $a:b:c = 0{\cdot}981:1:0{\cdot}908$, $\beta = 104°\ 16'$, biaxial, with principal refractive indexes $> 1{\cdot}780$, $2V = 75°$.[65] The corresponding dichloro compound forms thin, silky, reddish gold needles showing direct extinction; $n_\gamma > 1{\cdot}780$, $n_\beta > 1{\cdot}780$, $n_\alpha > 1{\cdot}778$. The dibromo compound is a yellow powder composed of crystals showing symmetrical extinction pleochroism with colour from deep to pale green; $n_\gamma \simeq 1{\cdot}780$, $n_\alpha = 1{\cdot}659$.

Polarographic investigation[48] indicates that the complex ions formed between zinc and hydroxylamine are $[Zn(NH_2OH)]^{++}$ and $[Zn(NH_2OH)_2]^{++}$; the formation constants were found to be $2{\cdot}5 \pm 1$ and $10{\cdot}2 \pm 2$ respectively, in solutions of unit ionic strength. No evidence was found for higher species of complex ions up to one-molar hydroxylamine concentrations.

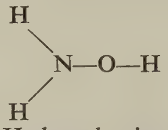
Another type of hydroxylamine complex is that formed with boron trifluoride. Thus hydroxylammonium chloride and boron trifluoride etherate yield at 60–100° the complex BF_3,NH_2OH[81] which has been considered to be NH_3OBF_3.

Formation of Sulphuric Acid Derivatives

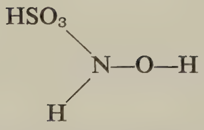
The extensive work of Raschig and others on the various sulphuric acids derived from hydroxylamine was dealt with in the original Treatise (Mellor, VIII, 302–3, 672–9). These derivatives fall into two classes, namely, those in which the SO_3H group replaces (i) any one or more hydrogen atoms, or (ii) the hydroxyl group.

(*Note*: The names assigned to the various compounds are based on Rule 3.33, I.U.P.A.C. Rules for Inorganic Nomenclature (1957). The names in parentheses are those used in Mellor, VIII, and in this section reference numbers in heavy type relate to the following compounds or their ions.)

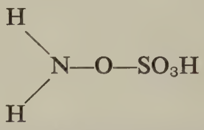
(i) In this group there are both N- and O-sulphuric acids:



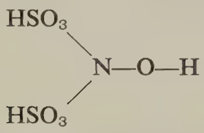
Hydroxylamine



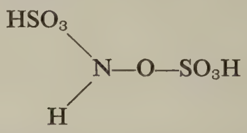
Hydroxylamido-N-sulphuric acid (**I**)
(Hydroxynitrilomonosulphonic acid)



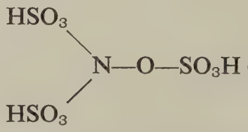
Hydroxylamido-O-sulphuric acid (**II**)
(Hydroxynitrilo*iso*monosulphonic acid)



Hydroxylamido-N,N-disulphuric acid (**III**)
(Hydroxynitrilodisulphonic acid)



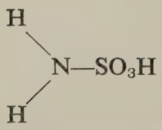
Hydroxylamido-N,O-disulphuric acid (**IV**)
(Hydroxynitrilo*iso*disulphonic acid)



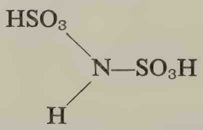
(**V**)

Hydroxylamido-N,N,O-trisulphuric acid
(Hydroxynitrilotrisulphonic acid)

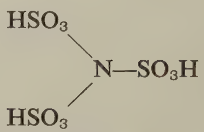
(ii)



Amidosulphuric acid (**VI**)
(Amidosulphonic acid)
(Trivial name: Sulphamic acid)



Imidodisulphuric acid (**VII**)
(Imidosulphonic acid)



Nitridotrisulphuric acid (**VIII**)
(Nitrilotrisulphonic acid)

The formation of potassium hydroxylamido-N,N-disulphate (**III**) has been observed during the reaction between hydroxylamine and the violet potassium nitrosyldisulphate.[84] The product was assayed by hydrolysis to hydroxylamine and titration with bromate. Since the product is colourless the reaction can be used for the titrimetric determination of either hydroxylamine or the nitrosodisulphate. The formation of hydroxylamido-N,N-disulphate ions (**III**) by the decomposition of nitrosyldisulphate ions was followed by chemical and spectrophotometric methods.[85] The results agreed with the equation:

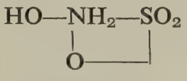
$$4(SO_3)_2NO^{--} + 7H_2O \rightarrow 2(SO_3)_2NOH^{--} + N_2O + 4SO_4^{--} + 4H_3O^+$$

The visible and ultra-violet absorption of potassium nitrosyldisulphate is determined and used to follow the rate of the reaction. Oxidation of potassium hydroxylamido-N,N-disulphate (III) by permanganate gives a 40–45% yield of potassium nitrosyldisulphate.[86]

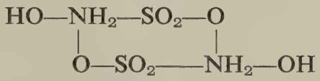
In the iron-catalysed reaction between hydroxylamido-N-sulphate (I) ions and nitrosyldisulphate ions, the disappearance of the latter was followed spectrophotometrically.[87] A mechanism was proposed based on the prior formation of $Fe(OH)^{++}$ and $Fe(OH)_2^{+}$, and their reaction with hydroxylamido-N-sulphate ions to give 'reactive products'. These products react with the nitrosyldisulphate ions to form nitrous oxide and hydroxylamido-N,N-disulphate ions(III), which are also formed by the reaction:

$$Fe^{++} + H_2O + ON(SO_3)_2^{--} \rightarrow Fe(OH)^{++} + HO.N(SO_3)_2^{--}$$

The product from the reaction between hydroxylamine and chlorosulphonic acid has been formulated as $O{:}NH_2SO_2.OH$ ('sulphamic acid N-oxide') and its stability, which is much greater than that of its salts, is attributed to its possession of an inner salt structure, thus:



or



The unstable salts have an open structure.[88]

The preparation of salts and esters of hydroxylamido-O-sulphuric acid (II) has been effected as follows.[89] The base or salt providing the cation is dissolved in ice-cold methanol (in some cases a little water is needed for complete solution) and added as a thin stream to a stirred solution of hydroxylamido-O-sulphuric acid in ice-cold methanol. The salt formed is collected (sometimes by adding benzene, ether or, for the silver salt, light petroleum), washed and dried *in vacuo*. Among the stable salts is the hydroxylammonium salt and among the unstable salts is the hydrazinium salt.

The reaction of sulphur trioxide in dry nitrogen with dry hydroxylamine gives hydroxylammonium sulphate containing about 2% of hydroxylamido-O-sulphuric acid.[90] If the reaction is carried out in nitromethane at $-20°$ the product contains about 30% of the sulphate and 70% of the acid. If hydroxylammonium salts are sulphonated with hydroxylamido-N,N,O-trisulphuric acid (V), then hydroxylamido-O-sulphuric acid is said to be produced in better yields and of higher purity.[91]

The literature on hydroxylamido-O-sulphuric acid (II) has been reviewed.[82, 83] Infra-red measurements indicate the presence of NH_3^+ and $-O-SO_2-O-$ groups and it is believed that the compound is an equilibrium mixture of $NH_2.O.SO_3H$ and $(NH_3)^+(OSO_3)^-$.

Amidosulphuric acid (VI) can be prepared from hydroxylammonium salts and sulphur dioxide; if the reaction is carried out under pressure the yield is considerably increased and the reaction time shortened.[92] The reaction is inhibited by excessive concentrations of hydronium ions and a mechanism based on co-ordination between the sulphur dioxide and hydroxylamine, followed by rearrangement, was proposed. This has been disputed[93] and the following competing reactions put forward instead:

$$H_2SO_3 + NH_2OH \rightarrow NH_2.SO_3H + H_2O$$
$$H_2SO_3 + NH_2OH \rightarrow H_2SO_4 + NH_3$$

The proportion of ammonia formed to hydroxylamine consumed and the dependence of the consumption of sulphite on the pH, were determined in the range pH 1–7. It was maintained that the detailed reaction mechanism cannot be decided by kinetic experiments since it cannot be held that reaction occurs between any one pair of the moieties NH_2OH, NH_3OH^+, SO_3^{--}, HSO_3^-, H_2SO_3 and dissolved SO_2. From the results obtained the hypothesis for formation of a negatively charged transition complex between NH_2OH and HSO_3^- was rejected.

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The hydrolysis of hydroxylamido-N,N,O-trisulphate (V) ion in perchloric acid has been shown, by the use of labelled sulphur, to give hydroxylamido-N,O-disulphate (IV) which is then hydrolysed much more slowly to hydroxylamido-O-sulphate (II) rather than hydroxylamido-N-sulphate (I)[94]:

$$(SO_3)_2N.O.SO_3^{3-} + H_2O \rightarrow SO_3.NH.O.SO_3^{2-} + HSO_4^-$$

$$SO_3.NH.O.SO_3^{2-} + H_2O \rightarrow NH_2.O.SO_3^- + HSO_4^-$$

$$NH_2.O.SO_3^- + H_2O \rightarrow NH_2.OH + HSO_4^-$$

Salts of hydroxylamido-N,N,O-trisulphuric acid (V) can be recrystallized from dilute acid although it is hydrolysed slowly in acid solution, finally giving hydroxylamine and sulphuric acid. The kinetics of the reactions have been studied and the following mechanism has been proposed:

$$^-O_3S.O.NR.SO_3^- + H^+ \rightleftharpoons {}^-O_3S.O.N^+RH.SO_3^-$$

$$^-O_3S.O.N^+RHSO_3^- \xrightarrow{\text{slow}} {}^-O_3S.NRH + SO_3$$

$$SO_3 + H_2O \xrightarrow{\text{fast}} H^+ + HSO_4^-$$

$$(\text{tri-, } R = SO_3^-;\ \text{di-, } R = H)$$

Reaction with Nitrites

The first step in the reaction between hydroxylamine and a nitrite was thought to be the formation of hydroxylammonium nitrite which then decomposed leading to hyponitrous acid or nitrosylhydroxylamine.[95, 96] Later work[97] indicated that free nitrous acid, rather than the nitrite ion, reacted with the hydroxylammonium ion. The proposed mechanism postulates the replacement of hydrogen in the latter ion by NO, followed by decomposition giving N_2O and H_3O^+:

$$NH_3OH^+ + HNO_2 \rightarrow HNO + HNO + H_3O^+$$

$$HNO + HNO \rightarrow H_2O + N_2O$$

$$HNO + HNO \rightarrow H_2N_2O_2 \text{ (about 1\%)}$$

Iodine or KI–HNO_2 is used as the indicator. It was found that the rate of reaction is increased by an increase in the concentration of either the iodine or the hydroxylamine. An increased concentration of sodium nitrite drastically retards the reaction, whereas the addition of potassium iodide slightly accelerates it. Hydrogen ions also catalyse the reaction, via the formation of iodine. These observations are accounted for by the following equations:

$$2NH_3OH^+ + 2I_2 \rightarrow 6H^+ + 4I^- + N_2O + H_2O$$

$$NO_2^- + I^- + 2H^+ \rightarrow \tfrac{1}{2}I_2 + H_2O + NO$$

The formation of hyponitrites was observed in the slow decomposition of hydroxylamine in alkaline solutions, in the absence of air and at room temperatures.[98] About 10% conversion into hyponitrite ion according to the equation:

$$4NH_2OH + 2OH^- \rightarrow 2NH_3 + 4H_2O + [N_2O_2]^{--}$$

takes place after several days. The first step is:

$$2NH_2OH \rightarrow H_2O + NH_3 + HNO$$

In alkaline solution the HNO produced reacts with the hydroxylamine to give nitrogen, a side reaction leading to $N_2O_2^{--}$ which decomposes to N_2O:

$$NH_2OH + HNO \rightarrow N_2 + 2H_2O$$

The main reaction in alkaline solution is thus:

$$3NH_2OH \rightarrow NH_3 + N_2 + 3H_2O$$

In acidic solution the HNO dimerises to $H_2N_2O_2$, which decomposes to N_2O and H_2O; however the main reaction here is:

$$4NH_2OH \rightarrow N_2O + 2NH_3 + 3H_2O$$

Miscellaneous Reactions

The reaction between hydroxylamine and dinitrosyl pyrosulphate has been compared with that of nitrosyl chloride.[99]

The exchange reaction of hydroxylamine and gaseous nitrogen has been studied with ^{13}N; the relative intensity of the hydroxylamine was found to be 5, compared with sodium nitrite 10, sodium nitrate 1, ammonium chloride, potassium cyanide, hydrazine sulphate 0·01.[100] With ^{15}N, however, no exchange could be detected with hydroxylammonium chloride.[101] (0·1 M. in water and 0·1 M. in N-free bacteriological culture medium buffered to pH 7·3.)

The formation of $KONH_2$ is postulated during the oxidation of KNH_2 by dry oxygen.[102] Salts of hydroxylamine can be prepared by double decomposition, the conditions being adjusted to the nature of the salt required. Thus, hydroxylammonium perchlorate can be prepared by the mixing of absolute ethanol solutions of hydroxylammonium chloride or sulphate and barium perchlorate. The precipitated barium salt is filtered off and the filtrate evaporated to dryness *in vacuo*. The residue can be purified by recrystallization from ether–benzene. The perchlorate, m.p. 87·5–90°, decomposes at 120° and is hygroscopic.[103] The phosphate, arsenate and oxalate can be prepared by precipitation from aqueous hydroxylammonium chloride by the addition of the appropriate acid and sodium hydroxide.[104] The low solubility of hydroxylammonium phosphate can be utilized in the recovery of hydroxylamine.[105] Thus the phosphate can be precipitated at pH 6–6·3, collected, washed with water and converted into the chloride by treating it with water, concentrated hydrochloric acid and hydrogen chloride at 80°. Hydroxylammonium salts of organic acids have been obtained by simple neutralization in ethanol.[106] These salts can also be obtained by the addition of an ammonium or alkali-metal salt of the acid to hydroxylammonium chloride or sulphate in methanol or ethanol at 40–70°.[107] Hydroxylammonium sulphate can be prepared from the hydrogen sulphate by the addition of the latter to 84·5–97·5% aqueous methanol, whereupon the required sulphate crystallizes.[108] In the solid state hydroxylammonium sulphate starts to decompose exothermally at 130° to 140°, producing ammonium bisulphate, m.p. 146·9°, which decomposes endothermally at 490° to nitrogen, oxygen, sulphur dioxide and water.[109] The corresponding chloride can be prepared by heating the sulphate, aqueous hydrochloric acid and a lower aliphatic alcohol to about 70° and cooling, when the chloride separates and can be collected.[110] When an anhydrous alcoholic solution of hydroxylamine, cooled in ice, is saturated with boron trifluoride a yellow solution is produced; addition of benzene to this solution causes a yellow oil to separate which crystallizes as colourless needles of hydroxylammonium fluoroborate, when cooled in ice.[111] The salt, which is extremely hygroscopic, melts over the range 45–60° and decomposes at ca. 150°. The mechanism of formation and *X*-ray absorption data were discussed.

The formation of hydroxyurea by the reaction of hydroxylammonium ion with cyanate ion has been the subject of a kinetic study.[112–114]

The inhibition of catalase by hydroxylamine has been investigated thermodynamically.[115, 116] Hydroxylamine also inhibits the Hill reaction[117] for the photochemical reduction of quinones etc. Hydroxylammonium chloride was observed to have a slight catalytic action on the reaction between palm oil and 94% ethanol,[118] whereas it does not alter the autodisplacement of lead into lead solutions.[119] The chemical stress relaxation of polyvinylformal by hydroxylammonium chloride has been measured at various concentrations.[120] Dihydroxylammonium sulphate was among a number of salts examined for their effect on the formation and degradation of sugars during the hydrolysis of polysaccharides.[121]

Refs. p. 140

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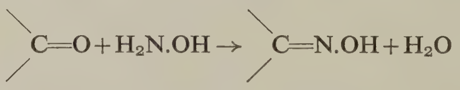
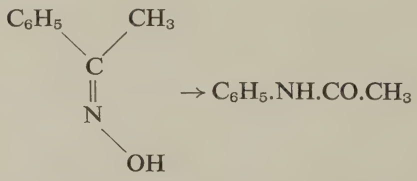
ORGANIC REACTIONS OF HYDROXYLAMINE

Hydroxylamine condenses with organic compounds containing a carbonyl group, with the elimination of water, to form an oxime:



$$>C{=}O + H_2N.OH \rightarrow\ >C{=}N.OH + H_2O$$

This is a very widely used reaction since the products are often crystalline and are useful for identification purposes.[1–7] The preparation, properties and chemical reactions of oximes have been discussed in detail.[8] Of particular interest is the stereoisomerism which is produced by those oximes having two different groups attached to the carbon atom, and which is due to the proximity of the hydroxyl group to one or the other of these groups.[8–11] The most common reaction carried out with oximes is the Beckmann rearrangement, which involves the migration of the group, *trans* to the hydroxyl group, from the carbon atom to the nitrogen atom together with the transfer of the hydroxyl group to the carbon atom, the final product usually appearing as an amide:



$$(C_6H_5)(CH_3)C{=}N{-}OH \rightarrow C_6H_5.NH.CO.CH_3$$

The Beckmann rearrangement has been reviewed at length.[12]

The mechanism and rates of reaction of the condensation of hydroxylamine with various types of carbonyl compounds have been examined.[13–19] The greater reactivity of the carbonyl group compared with the mercapto group was demonstrated by the reaction of hydroxylamine with α-mercaptobenzalacetophenone.[20] In the reaction between hydroxylamine and 2-bromo-*cyclo*pent-4-en-1-one, elimination of hydrogen bromide occurred to give the oxime of *cyclo*penta-2,4-diene-1-one as the first product.[21] Two molecules of this product added together in Diels–Alder fashion, one molecule acting as dienophile.

The formation of oximes has been developed as a micro-method for the determination of the carbonyl group.[22]

Instead of the hydroxylammonium salts usually used, hydroxylamido-disulphates have also been employed for the preparation of oximes from carbonyl compounds.[23] The method is also used to prepare hydroxylammonium salts from the hydroxylamido-disulphates, since the former can be recovered from the oximes by distillation with the appropriate acids.

In a reaction analogous to the formation of oximes from carbonyl compounds, hydroxylamine reacts with thiocarbonyl compounds with the elimination of hydrogen sulphide.[24]

Oximes have also been prepared by the action of hydroxylammonium salts on *iso*nitriles,[25] acylals,[26] nitrosophenols[27] and, along with phenols, from aryl or *cyclo*-alkyl hydroperoxides.[28] Excess of hydroxylamine solutions in methyl alcohol converts pure nitriles or commercial mixtures of cocoa, soyabean or tallow nitriles into amido-oximes.[29] These compounds ($\geqq 6$C) are soluble in various organic solvents and permit the extraction of $AuCl_4^-$, Co^{++}, Ni^{++}, $PdCl_4^{--}$, $PtCl_6^{4-}$, $RuCl_6^{--}$ and UO_2^{++} from aqueous solution.

Reduction of pyridine with sodium and ethanol affords 1,4-dihydropyridine which, with two equivalents of hydroxylamine, yields the dioxime of glutaric dialdehyde in an overall yield of 90%.[30] Some cyclic vinyl ethers also give oximes when treated with hydroxylamine.[31]

The hydrogenation,[32, 33] oxidation[34] and polarography[35, 36] of oximes have been investigated.

O-Benzoyl hydroxylamine has been prepared by the action of *p*-nitrophenyl benzoate on hydroxylamine,[37, 38] and by the benzoylation of *tert*-butyl N-hydroxycarbamate (which is prepared from hydroxylammonium chloride and $N_3.CO_2.CMe_3$), followed by acidic hydrolysis.[39] Acetic anhydride converts hydroxylammonium chloride into N,N,O-triacetyl and N,O-diacetyl derivatives.[40]

Hydroxylamine also reacts with esters, amides, lactones and anhydrides with the formation of hydroxamic acids, e.g. R.C(OH):NOH. Hydroxamic acids form coloured compounds with several ions; in particular a cherry-red compound is formed with ferric ions and this reaction forms the basis of the well-known hydroxamic acid test for esters and the like. A kinetic study has been made of the hydroxylaminolysis of lactones.[41] Hydroxylamine also reacts with keto-lactones,[42] carbonyl compounds containing a sulphonic acid group,[43] dimethylaminoformyl chloride,[44] sulphinic acids,[45] nitro*cyclo*hexane,[46] saccharin,[47, 48] diacylamides,[49] mercaptans,[50] diethyl phthalate,[51] thiophen and formaldehyde,[52] quinazolines,[53–55] aniline and chloral,[56] organic peroxides,[57] dicarboxylic acid derivatives,[58] and *iso*diazotates.[59] Hydroxylamine reacts with perfluoro-olefins to give unstable products which lose hydrogen fluoride and yield fluorides of hydroxamic acids.[60] Chloro- and nitro-derivatives of phenoxy- and naphthyl-hydroxamic acids, nicotino- and *iso*nicotino-hydroxamic acids give coloured compounds with Cu^{++}, UO_2^{++}, Ni^{++}, Co^{++}, V^{5+} and Fe^{3+}.[61] In the colorimetric determination of penicillin, at 470–500 mμ, by the ferric hydroxamate method, the complex is stabilized by extraction with *iso*-butanol.[62]

From a mixture of hydroxylammonium chloride, hydrogen peroxide and benzene, *o*-nitrosophenol has been isolated.[63]

In the presence of sodium ethoxide, hydroxylamine and nitrobenzene react to give nitrosophenylhydroxylamine, $C_6H_5.N(O){:}NOH$.[64]

Hydroxylammonium chloride forms a salt with aqueous sodium dehydroepiandrosterone sulphate.[65]

When formaldehyde and hydroxylamine are heated together, a mixture of several amino-acids, hydroxy-acids and other compounds is produced.[66] The predominant amino-acid is glycine and the reactions are of significance in relation to the formation of biochemical compounds from simple carbon and nitrogen compounds, under conditions similar to those assumed to have existed during the early development of the earth's crust. Glycine is also produced by the electrolysis of a mixture of oxalic acid and hydroxylammonium sulphate.[67]

A useful reaction of hydroxylamine is found in the direct amination of aromatic compounds.[68, 69] This process can also be accomplished by the use of hydroxylamido-O-sulphuric acid,[70] which is also used in a general method for the preparation of mono- and 1,1-di-alkyl and 1,1,1,-trisubstituted hydrazines,[71] e.g.:

$$2C_6H_5.NH_2 + NH_2.O.SO_3H \rightarrow (C_6H_5.NH.NH_3)^+(C_6H_5.NH_3)^+SO_4^{--}$$

The hydroxylamido-O-sulphuric acid was prepared, in 82% yield, by the action of oleum on dihydroxylammonium sulphate.[71] Arylamines can also be prepared by the action of hydroxylamine and polyphosphoric acid on aromatic carboxylic acids.[72]

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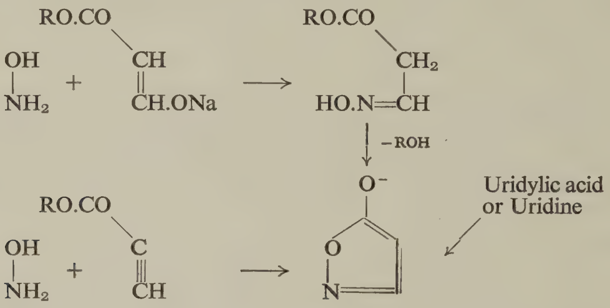
In the presence of aqueous sodium hydroxide, at room temperatures, hydroxylammonium chloride and Cl.CO.O.CH_2.C_6H_5 react to give N,N,O-tribenzyloxycarbonyl-hydroxylamine.[73] In the presence of potassium carbonate however, at 0° initially, hydroxylammonium chloride and ethyl chloroformate yield N-ethoxycarbonyl-hydroxylamine.[74]

Hydroxylamine will add to activated multiple bonds to give N-substituted compounds. Thus hydroxylamine adds to $\alpha\beta$-unsaturated acids to give 50–60% yields of N-derivatives.[75] Hydroxylamine is superior to hydrazine for the inactivation of biologically active nucleic acids; the following reactions were also carried out[76]:



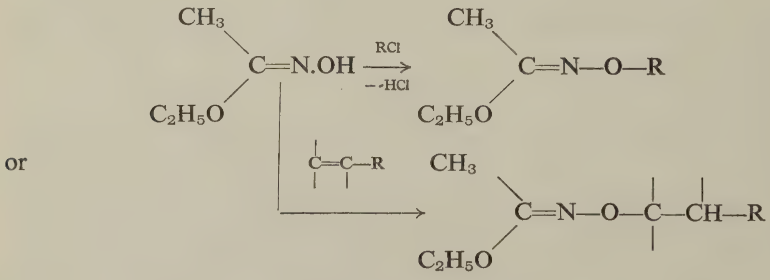
*iso*xazolone-5
(Stable only as the anion)

Other products were urea
and ribose oxime.

N,N-Disubstituted hydroxylamines add to activated double bonds to give O-alkylated products.[77]

The formation[78–83] and properties[84–89] of N-arylhydroxylamines have been widely studied.

The preparation and reactions of O- and N-alkyl and *cyclo*alkyl hydroxylamines have also been studied extensively, particularly in the last decade.[90–102] A recent method for the synthesis of O-substituted hydroxylamines involves the alkylation of ethyl acethydroximic acid:



Treatment of the O-alkylated product with acid yields the salt of the O-substituted hydroxylamine.[103]

Hydroxylammonium chloride has been used as a catalyst in the *cis* → *trans* rearrangement of azobenzene[104]; and for the reduction of aromatic seleninic acids.[105]

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APPLICATIONS

AS CORROSION RETARDANT

The oxidation–reduction properties of hydroxylamine are of use in combating corrosion, but substituted hydroxylamines have usually been found more effective. Thus a rust-inhibiting material can be made by the addition to an oil of 0·001 to 0·5% of hydroxylamine derivative, such as $RR'N.OH$, or a salt such as $R''_3N(OH).O.CO.R'''$, where R, R′, R″, and R‴ are hydrogen, hydrocarbon residues, etc.[1] Ferrous surfaces can be given increased corrosion-resistance and paint adhesion by treating them with phosphoric acid or alkali metal phosphates containing 0·1 to 0·5% of a hydroxylammonium salt followed by chromic acid,[2,3] or with chromic acid and a reducing agent such as hydroxylamine.[4] The addition of 0·2 to 12% of a water-soluble inorganic hydroxylammonium salt and 13 to 35% of an alkali-metal silicate to a detergent composition is said to inhibit tarnishing of copper and copper–nickel alloys.[5] A hydroxylamine–oxalate complex of chromium, $[Cr(HCO_2)_6][NH_4(NH_2OH)_2]$, has been used in a chromium electroplating bath.[6] The corrosion of manganese cathodes can be inhibited by the addition of hydroxylammonium sulphate to the electrolyte; in addition the current efficiency is increased.[7] The electrodeposition of manganese was found to need a reducing solution, and the effect of hydroxylamine as a possible reducing agent was studied.[8] The addition of reducing agents such as hydroxylamine inhibited the contamination of cathodic precipitates by mercury during the electrolysis of amalgams.[9] The effectiveness of organic hydroxylamine derivatives in producing corrosion resistance is attributed to their reducing effect towards atmospheric oxygen.[10] The addition of hydroxylammonium nitrate to a nitric–hydrofluoric acid mixture increased the corrosion rate of stainless steel from 2·5 to 465 mils/year.[11] Hydroxylammonium salts have been used in non-corrosive fluxes for soldering and metal coating.[12–14]

AS STABILIZER

Hydroxylammonium chloride (0·1%) considerably reduces the rate of oxidation of acrolein (only slightly at first), benzaldehyde and styrene.[15] Hydroxylammonium chloride has been used to stabilize solutions of polythionates[16] and concentrated formaldehyde solutions.[17] Hydroxylamine can be used to purify alcohols containing oxidizable impurities[18] and to remove free chlorine from hydrochloric acid.[19] In an example the concentration of free chlorine was reduced from 85 p.p.m. to 1 p.p.m. by the addition of 0·01% of hydroxylammonium chloride, followed by agitation for one hour.

Discoloration of polychloroprene on exposure to sunlight can be prevented by the addition of O-substituted hydroxylamines to the mixture before curing.[20] Hydroxylammonium chloride removes the colour from solutions of polyacrylonitrile or polymers containing at least 85% of the latter.[21] A mixture of formaldehyde, hydroxylammonium sulphate and an inorganic acid has been used to inhibit colour formation in acrylonitrile polymers.[22] Plasticizers having improved colour properties can be prepared by esterification in the presence of certain hydroxylamines.[23] The addition of 0·1% of hydroxylammonium chloride to 2-methyl-5-vinyl-pyridine and other vinylpyridines inhibits colour formation which occurs in sealed containers at 75°F.[24] Hydroxylamine is effective in preserving the vitamin *C* content of frozen strawberries, but in the presence of sugar the vitamin *C* content decreases.[25] The addition of 0·5% of hydroxylamine is effective in preventing the browning of the white meat of canned crab and squid meat.[26]

AS CATALYST

Hydroxylamine, in combination with hydrogen peroxide, catalyses the emulsion polymerization of olefinic and acetylenic compounds.[27, 28] The resin so obtained from vinyl chloride is unstable towards heat.[28] Hydroxylammonium chloride has been used as a catalyst in telomerization (polymerization) reactions between aldehydes or ketones (containing an alpha-hydrogen atom) and olefines.[29] Foam rubber can be produced by the addition of hydrogen peroxide and a catalase preparation, inhibited by a small amount of hydroxylammonium salt, to creamed latex.[30] A combination of hydroxylamine and 4-hydroxyl-biphenyl was tested, inter alia, as a stopping agent (polymerization inhibitor) for cold rubber.[31] Resorcinol and furfural react together to a certain extent at 85–110°, and further condensation can be brought about by dissolving the product in ethyl methyl ketone and adding hydroxylammonium chloride as a catalyst.[32] The product, when mixed with a solution of vulcanizable natural or synthetic rubber, gives an adhesive suitable for joining rubber to itself or to metals.

Hydroxylammonium chloride has been used as the catalyst in the manufacture of vinylacetylene,[33] and in the reaction between sulphur dioxide and olefines.[34]

Silver catalysts, used in the oxidation of ethylene to ethylene oxide, when poisoned by chlorine, hydrogen sulphide or sulphur dioxide, can be reactivated by soaking them in an aqueous solution of a hydroxylammonium salt.[35]

Hydroxylamine has been studied extensively as an anti-oxidant in photographic colour-developers.[36–41] In a mixture containing diethyl-*p*-phenylenediamine, sodium sulphite and potassium carbonate, the addition of hydroxylamine retards the rate of loss of the diamine but increases the rate for the sodium sulphite.[36] Copper ions increase the loss of the diamine but can be sequestered by Trilon-*B*; in a copper-free solution, however, Trilon-*B* decomposes the hydroxylamine which leads to an

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increase in the loss of the diamine.[37] The presence or absence of hydroxylamine is said to have only a secondary effect on the dependence of colour development on developer concentration.[41] Substituted hydroxylamines represented by the formula, $RR'R''CN(R''')OH$, where R is acyl, ester, acid, etc., R′, R″, R‴ are hydrogen, hydrocarbon or heterocyclic residues, or where $R'+R''$ is oxygen, have been patented for addition to colour-developers as stable anti-oxidants in place of the unstable hydroxylamine.[42] The processing of photographic paper is speeded up by using accelerators in the silver halide emulsion and using an alkaline solution of hydroxylammonium chloride as the developing medium.[43] Hydroxylamine, in less than 0·2% concentration, has been used as an antioxidant in diazotypes.[44]

IN THE DYEING INDUSTRY

The mild reducing properties of hydroxylamine find wide use in the dyeing industry. Hydroxylamine and hydroxylammonium salts are the preferred reducing agents in the dyeing of 'Orlon' acrylic fibres by the copper method.[45–47] In this method the acrylic fibre and the dye are treated, near the b.p., with a mixture of a cupric salt and hydroxylammonium sulphate; the cuprous ions produced bond to the fibre and salt formation then occurs with the dye anion. Over-reduction to metallic copper is avoided by the use of hydroxylamine[48] or hydroxylamine-based reducing agents.[45–47] The dye yield is said to be increased if the process is carried out at high temperatures (120–130°).[49] If dyed polyvinylpyrrolidinone-containing polyacrylic fibres are treated with a cupric sulphate–hydroxylammonium sulphate solution their colour fastness is improved.[50] The mechanism of the copper process has been discussed.[51] The cuprous ion is said to co-ordinate with the nitrile groups and thus introduce new positively charged sites at which absorption can occur. Hydroxylammonium sulphate is preferred for the reduction of cupric sulphate to cuprous ion at high temperature, since it has a slow action and, moreover, shows almost the theoretical oxidation–reduction potential. Polymeric nitriles, in the form of fibres, films, filaments, yarns (knitted or woven), or loose or fabricated threads, when treated with hydroxylamine or hydroxylammonium salts, under varying conditions of temperature and solvent, are converted into a much more readily dyed form.[52–65] The kinetics of reaction between hydroxylamine and powdered polyacrylonitrile in water have been studied.[66, 67] Adjacent amido-oxime groups appear to remain free and not to interact to form glutaro-imidedioxime rings; the results of physical measurements were compared with those for glutarodiamidoxime.[66] It has been argued that the improved dyeability of the polynitrile fibres is due to the intermediate formation of hydroxamic acid groups.[68] Amidoximation has also been used with partly cyanoethylated cotton fabrics (3–5% N)[69] and partly cyanoethylated polyvinyl alcohol fibres.[70] The advantages claimed include a considerable increase in the crease and flex resistance and moisture regain as well as increase in the affinity for acid, basic vat and disperse dyes.

Hydroxylammonium chloride, sulphate and thiocyanate find wide application in the development of leuco-sulphuric acid esters, i.e., of leuco vat print pastes.[71]

Other applications in the dye industry use the aminating properties of hydroxylamine compounds. Thus, dibenzanthrone in sulphuric acid, when treated with hydroxylammonium sulphate in the presence of ammonium molybdate, gives a product capable of dyeing cotton, from a blue vat, strong green-grey to black shades.[72] Polynuclear organic compounds containing at least one CO or CN group can be aminated or iminated by hydroxylamine or its compounds, in molten aluminium chloride, to give dyes or dyestuff intermediates.[73] In the presence of a catalyst hydroxylamine reacts with acedianthrone to give amino derivatives, acylation of which gives vat dyes yielding reddish brown shades of good fastness.[74]

MISCELLANEOUS USES

Tri-*n*-butyl phosphate is a satisfactory solvent for the extraction of cerium(IV) nitrate; re-extraction of the cerium with water or dilute nitric acid is, however, slow

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and laborious and a quicker, quantitative extraction can be achieved by reduction of the cerium(IV) to cerium(III) with hydroxylamine etc.[75] The separation of plutonium from uranium can be achieved in a 20% tri-*n*-butyl phosphate diluent system by countercurrent extraction with 0·1 M. $NH_3OH.NO_3$ (soltrol as diluent), which reduces the plutonium(IV) to plutonium(III).[76]

Hydroxylamine has been used to produce magnetites from basic 'ferro-ferrites', but is less effective than the nitrate ion.[77]

The ability of hydroxylamine to react with carbonyl compounds is utilized in the removal of minor amounts of methyl vinyl ketone from acrylonitrile.[78]

The addition of hydroxylammonium chloride to acrylonitrile polymer and copolymer solutions significantly lowers the viscosity which, in turn, leads to increased spinning speeds.[79] Acrolein polymers can be reacted with a hydroxylamine to give high molecular-weight derivatives.[80]

The relative position of hydroxylammonium ions in the selectivity scale for Dowex 50 resins has been reported[81] and preparations of ion-exchange resins selective for nickel incorporating hydroxylamine-derived groups have been described.[82–84] Resins which are highly selective for Fe^{+++}, but not for Zn^{++} or Cu^{++} (relative to H^+), were prepared by causing methacrylic acid polymers cross-linked with divinyl benzene to react with thionyl chloride and then with hydroxylamine.[82]

The use of hydroxylammonium chloride as coagulant for silicate suspensions in the production of phosphor screens has been described.[85] Treatment of bleached sulphite pulp with aqueous hydroxylammonium chloride indicates that the pulp undergoes some degradation; hydroxylammonium chloride/pyridine increases the viscosity.[86]

Hydroxylamine[87] and hydroxylammonium chloride[88] were among a large number of compounds examined for their depilatory action; on wet-salted hide soaked in lime liquor the observed accelerating effect was correlated with the structure of the compound rather than its basicity.[88]

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ANALYTICAL

Qualitative Detection

Hydroxylamine enters into several reactions which are distinguished by the formation of characteristic colours or precipitates. The degree of sensitivity varies very widely, the utility of the reaction for the detection of hydroxylamine varying accordingly.

If a solution containing 0·0001 g./l. of hydroxylamine is made alkaline and to it is added a specified mixture of α-naphthol and *p*-bromonitrosobenzene an orange-yellow colour results[1, 2]; if 1–2 drops of a solution of a magnesium salt are also added the colour reddens and the test becomes more sensitive. The following reagents were also tried, the figures in parentheses representing the sensitivity in g./l.: (i) sodium nitroprusside (0·1), (ii) benzoyl chloride and ferric chloride (0·005), (iii) diacetyl monoxime and nickel (0·002), (iv) ammonium sulphide, ammonium hydroxide and alcohol (0·002), (v) ammonium sulphide, ammonium hydroxide and manganese sulphide (0·00047), (vi) the Griess reagent (0·000003). In using the last reagent small quantities of thiosulphate interfere with the colour reaction.[3] If a solution containing 1 p.p.m. of hydroxylamine or hyponitrous acid is treated with a citrate buffer, followed by a resorcinol–iodate reagent, a cherry-red colour develops in 3–15 minutes.[4]

If hydroxylamine or an N-alkyl hydroxylamine is acidified and treated with sulphanilic acid followed by iodine solution until a brown colour results and thiosulphate is added to decolorize the solution, the addition of α-naphthylamine in aqueous acetic acid gives a red colour.[5] Hydroxylammonium chloride gives a colour reaction with phosphomolybdic acid.[6] The ammonia liberated when hydroxylamine oxidizes ferrous hydroxide to ferric hydroxide blackens a solution containing manganous and silver ions; this reaction can be used to detect as little as 0·1 γ of hydroxylamine.[7] In a study of the detection of hydroxylamine, hydrazine and their mixtures the former was detected by the evolution of ammonia when boiled with sodium carbonate, glucose and ferrous sulphate; when the evolution of ammonia ceased the hydrazine present was converted into ammonia by the addition of sodium hydroxide and again boiling the solution.[8]

A very sensitive test for hydroxylamine is provided by its reaction with 8-hydroxyquinoline ('oxine').[9] Initially, 5-amino-8-hydroxyquinoline is formed, which is oxidized by atmospheric oxygen to 5,8-quinolinequinone-5-(8-hydroxyquinolylimide) and this product colours the reaction mixture green; the limiting concentration is 1:12,000,000 or 0·08 γ/ml. hydroxylamine. In the presence of large amounts of hydroxylamine a brown precipitate sometimes separates. The test works in the presence of ammonia but large amounts of hydrazine reduce the sensitivity or inhibit it completely.

The addition of hydroxylamine to sodium pentacyanoammineferrate, $Na_3[Fe(CN)_5NH_3]$, gives a feeble yellow solution which gives a deep pink colour with aniline; in the absence of the hydroxylamine a greenish colour is produced.[10]

Several procedures have been described for the detection of hydroxylamine by means of 'spot tests'. Thus hydroxylamine may be oxidized by iodine and the nitrous acid so formed may be detected by the Griess test.[11] The reaction of hydroxylamine with salicylaldehyde and cupric ions has been used as a spot-test.[12] A spot-test depending on the formation of molybdenum blue can serve to distinguish between hydrazine and hydroxylamine.[13] When an ammoniacal solution of hydroxylamine is added to ammoniacal cupric ferro- or ferri-cyanide, a white precipitate of the cuprous salt appears; by this means 0·2 μg. hydroxylamine, at a dilution of 1:250,000, can be detected (also 0·3 μg. hydrazine at 1:150,000 and 0·5 μg ascorbic acid at 1:100,000).[14] If a few drops of a saturated acetone solution of *p*-dimethylaminobenzylidenerhodanine are added to the clear blue solution formed by the addition of N. $Na_4P_2O_7$ dropwise to 0·5 N. $CuSO_4$, then the resulting reagent, which gives a red or orange-red spot and keeps for half a day, is very sensitive to hydroxylamine, hydrazine or ascorbic acid.[14] Test papers impregnated with PbO_2, Tl_2O_3 or other higher oxides also form efficient detectors of these three reducing agents.[14] The previously described formation of ferric hydroxamate from hydroxylamine has been used as the basis for a spot test which is sensitive to 0·1 μg. of hydroxylamine at a limiting concentration of 1:50,000.[15]

The presence of ammonium salts, NH_4X, in hydroxylammonium salts can be detected by their conversion into hexamethylenetetramine and HX, by treatment with formaldehyde. The liberated HX can be titrated with sodium hydroxide.[16]

Paper chromatography has been used to separate and identify gamma quantities of hydroxylamine and hydrazine, using the colours formed with picryl chloride and other reagents.[17] The paper chromatographic separation of ammonium chloride, hydrazine, hydroxylamine, phenylhydrazine and N-phenylhydroxylamine has been described.[18] The resolution of freshly prepared 2 N. NaOH solutions of NaN_2O_2 with sodium nitrite, sodium nitrate or dihydroxylammonium sulphate has been effected by downward chromatography on Whatman No. 1 paper; aqueous ethanolic sodium hydroxide was used as the eluant and the hyponitrite appeared in the upper sodium hydroxide zone, with a relative R_f value of 0·1, whilst the aqueous ethanol moved the nitrite, nitrate and hydroxylamine downwards with a relative R_f of 0·5–0·6.[19] Paper ionophoresis[20] on Whatman No. 1 paper has been used to separate mixtures of ammonia, hydroxylamine, hydrazine, hyponitrite, nitrohydroxylamate, nitrite and nitrate; the first three were developed by 0·5% K_2HgI_4 in 2·5% NaOH.

Quantitative Determination

Hydroxylamine and hydrazine can be determined, in the presence of each other, by the determination of the total reducing content by the bromate method, and then, after the hydroxylamine has been reduced with ferrous ion, the hydrazine content can be found by iodate titration.[21] The fact that hydroxylamine is reduced by alkaline ferrous sulphate, whereas hydrazine is not affected, has been developed into a method for the determination of the former in the presence of the latter, by the determination of the ammonia evolved.[22] Micro-methods for the determination of hydroxylamine, nitrite, nitrate and their mixtures have been given.[23] A study of the methods applicable to solutions containing sulphuric acid, acetone and sometimes ammonia, indicated that the Raschig method (1887) of titration with ferric ion was preferable to the Staehler method (1904), which uses titanous ion.[24] Hydroxylamine can be determined by treatment with an excess of standard ferric alum and back titration with standard mercurous nitrate solution.[25] *cyclo*Hexanone oxime, both pure and crude, can be determined by hot acidic hydrolysis to hydroxylammonium sulphate and titration of the latter with ferric alum in the presence of an excess of titanium trichloride and carbon dioxide.[26] In the presence of aqueous cupric sulphate and the absence of mineral acids, ferric salts rapidly oxidize hydroxylammonium chloride, at room temperature, to nitrous oxide; after the addition of sulphuric acid the ferrous ion produced can be determined with sodium vanadate, using diphenylamine sulphonate as the indicator.[27] Alkaline ferricyanide completely oxidizes hydroxylamine to nitrogen; the analysis can be completed either by the titration of the ferrocyanide with ceric sulphate,[28] or by the addition of potassium iodide and zinc sulphate followed by titration with arsenite or, after acidification, with thiosulphate.[29] This method of oxidation has been utilized in the determination of milligram amounts of hydroxylamine and hydrazine in a mixed sample.[30]

Hydroxylammonium chloride can be determined by the addition of an excess of standard iodine solution to a borax–boric acid buffered solution, followed by back-titration with standard arsenious oxide solution.[31] In a mixture of acetoxime and hydroxylamine, only the latter is oxidized by iodine and can thus be determined iodometrically; this observation was employed in a study of the hydrolysis of acetoxime.[32] Hydroxylamine can also be determined by the addition of an excess of iodine monochloride and back-titration with hydrazine.[33, 34]

The reaction between bromine and hydroxylamine has been shown to give nitric and hydrobromic acids quantitatively[35] and satisfactory results have been obtained by the electrolysis of a hydroxylamine solution, containing not more than 0·008 g. of hydroxylamine, in the presence of potassium bromide until an excess of bromine was present; this excess was determined iodimetrically and the silver deposited in the coulometer also determined.[36] When hydroxylammonium chloride is caused to react with bromine, eight equivalents of acid are produced according to the equation:

$$NH_3OH.Cl + 3Br_2 + 2H_2O \rightarrow HNO_3 + HCl + 6HBr$$

These eight equivalents can be determined by the aeration method with methyl red as indicator, or by the ferrocyanide method with either methyl red or phenolphthalein as indicator.[37]

If an excess of standard ammonium tetrasulphatocerate is added to hydroxylamine either as the sulphate or chloride, the excess can be determined by back-titration with arsenious acid, after the addition of a catalytic amount of osmium tetroxide.[38] Hydroxylamine can be determined by dissolving it in methyl alcohol and titrating the solution with ammonium hexanitrato-cerate in the presence of aqueous nitric acid as catalyst.[39] The colour change, from strong orange-red to yellow, has also been used as the basis of a colorimetric method.[39]

Several methods for the vanadimetric determination of hydroxylamine have been described. For example, if an excess of acidic vanadate is added to a hydroxylamine solution then, after 20–30 minutes, the excess of vanadate can be titrated with Mohr salt solution.[40] The action of the acidic vanadate is catalysed by cupric sulphate and after 10 minutes the excess of vanadate can be titrated with ferrous sulphate, using N-phenylanthranilic acid as an indicator.[41] Hydroxylamine can be determined by the addition of an excess of vanadium(II) sulphate in sulphuric acid; the solution is heated to 95–100° for three minutes and then the excess can be determined by titration with a ferric solution to a phenosafranine end-point.[42] The solution of vanadium(II) can be prepared by the reduction of vanadium(V) with zinc amalgam,[43, 44] or with zinc and sulphuric acid.[44] In a review on vanadimetry the determination of hydroxylamine was included.[45]

Two procedures for the determination of hydroxylamine using molybdates have been published. In the first of these acidic sodium molybdate is reduced to molybdenum(III) by zinc amalgam, the hydroxylamine solution together with sodium vanadate is added and the solution heated to 100° for 10–15 minutes; the excess of molybdenum(III) is titrated with potassium permanganate.[46] The second method uses ammonium molybdate and a sensitivity of 6·6 mg./ml. is claimed.[47]

A method for the direct titration of hydroxylammonium salts, in aqueous acetone, with sodium hydroxide has been described.[48] This method has been modified so as to enable it to be used for the titration of technical solutions in the presence of dihydroxylammonium sulphate and free sulphuric acid.[49] The liberation of hydrochloric acid by the addition of formaldehyde to hydroxylammonium chloride, at pH 3·9, has been used as the basis for the determination of hydroxylamine and its salts in the colour developers; 0·05 N. sodium hydroxide is used to estimate the liberated acid.[50, 51]

Several reactions of hydroxylamine lend themselves to its determination by colorimetry. Thus, ketoximes form intensely blue chloro-nitroso compounds when treated with chlorine (from chlorinated urea); hence hydroxylamine can be determined colorimetrically by its reaction with *cyclo*hexanone, in an acetate buffer, in the presence of chlorinated urea.[52] Diazotized sulphanilic acid forms a characteristic dye with α-naphthylamine which can be used for the colorimetric determination of nitrous acid or compounds which can be converted into nitrous acid. Thus if hydroxylamine is oxidized, with iodine–acetic acid, to nitrous acid in the presence of sulphanilic acid and α-naphthylamine a colour is produced, the intensity of which is dependent on the hydroxylamine concentration.[53] Similarly oximes can be determined after hydrolysis and oxidation to nitrous acid.[53] The formation of the above dye is also used to determine nitrite, hydroxylamine and nitrate in the presence of each other.[54, 55] The nitrite is determined first and then, in a separate experiment, it is removed by the thermal decomposition of the diazotized sulphanilic acid; the hydroxylamine can then be oxidized to nitrite by iodine and, after removal of the excess of iodine with thiosulphate, the nitrite produced can be determined as before; the limiting concentration of hydroxylamine is 5×10^{-7} mole/l. A procedure, based on the formation of the above dye, has been published for the determination of aqueous mixtures of nitrous acid, hyponitrous acid, hydroxylamine and ammonium hydroxide.[56] The differential determination of hydroxylamine and β-aspartylhydroxamate in their mixtures has been achieved by oxidation at pH 2·3, when only the former is oxidized, and also at pH 3·7 when both compounds are oxidized. The resultant nitrite solutions can be determined colorimetrically with the aid of α-naphthylamine and sulphanilic acid.[57] The reaction of hydroxylamine with 8-quinolino[9] has been developed into a photometric method for the determination of 0·2–100 μg. of hydroxylamine; details are given for the determination of the hydroxylamine produced by the hydrolysis of *cyclo*hexanone oxime.[58] If a developer solution (20 ml.), containing hydroxylamine, is shaken with aqueous sodium hydroxide (4 ml., 10%) and ethyl acetate (1 ml.), acidified with nitric acid (20 ml., 25%) and diluted with water to 400 ml., then the addition of ferric chloride (1 ml., 30%) to the solution (200 ml.) gives a red colour, the extinction of which can be measured in a colorimeter; over the range 0·2–1 g./l. hydroxylammonium sulphate the Lambert–Beer law is obeyed.[59] Ferric ion reacts with formohydroxamic acid, from hydroxylamine, formaldehyde and persulphate, to give the coloured $Fe(HCO.NOH)_3$; solutions containing 20–200 μg./ml. hydroxylamine obey the Lambert–Beer law.[60] Tartaric acid and citric acid deepen the colour and several other substances interfere. A method has been published for the colorimetric determination of hydroxylamine by the addition of aqueous picric acid and 1% sodium hydroxide, followed by measurement at 525 mμ.[61] For accurate measurement a final concentration of hydroxylamine of 0·5–8 μM. is required. In a presentation of spectrophotometric data, suitable for the systematic identification of dangerous drugs, poisons and narcotics, the optical density at 298 mμ of hydroxylamine was given as nil in acidic solution and 0·002 in alkaline solution (computed for 1 p.p.m., i.e., 1 μg./ml.).[62]

The oxidation of hydroxylamine by ammoniacal cupric sulphate at 90° can be followed potentiometrically, a sudden drop in the potential occurring at the end-point.[63] Direct potentiometric titration of hydroxylamine can also be achieved with potassium ferricyanide,[64] and with cupric acetate.[65] In the latter case the mean error has been quoted as ±0·46%. The potentiometric titration of ammonia and hydroxylamine in the presence of polymeric hydroxamic acids has been described.[66] Amperometric titration of hydroxylamine with titanium trichloride in aqueous oxalic acid at 50° (dropping mercury electrode) or with potassium bromate in hydrochloric acid in the presence of potassium bromide at 60–70° (rotating platinum electrode), has been accomplished.[67]

The polarographic determination of hydroxylamine at pH 6–7 allows 10^{-4} M. concentrations to be determined, but at pH 3–4 concentrations of 10^{-3} M. are required.[68] In a study of the equilibria in the reactions between hydroxylamine and ketones, the polarographic determination of free hydroxylamine was said to be superior to other methods such as iodimetric or colorimetric determinations.[69] It has also been said that hydroxylamine itself is not polarographically reproducible but can be determined indirectly via the oximation reaction with *cyclo*hexanone.[70] Polarographic analysis of hydroxyurea, m.p. 72°, showed that it was not identical with hydroxylammonium cyanate.[71]

Hydroxylammonium oxalate and chloride are oxidized, in neutral solution, by potassium permanganate quantitatively to nitrogen and nitrous oxide.[72] With the oxalate some carbon dioxide is also produced which must be absorbed before the gas volumes are measured; the method is said to be precise to 0·5%.

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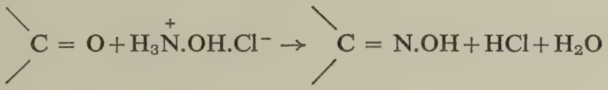
Ferric salts form characteristic dark cherry-red solutions with hydroxamic acids and since the latter can be made by the action of hydroxylamine on esters, lactones and anhydrides, the reaction has been developed into a means of recognizing these types of compound. Thus the following method has been described for the recognition of esters and/or lactones.[73] A stock solution is made up from hydroxylammonium chloride (70 g.), thymolphthalein (0·2 g.) and methyl yellow (0·1 g.) in methyl alcohol (1 litre); the sample is treated with 1 ml. of the test solution, made alkaline with methyl alcoholic potassium hydroxide (2 M.) and then boiled for ½ min. Methyl alcoholic hydrogen chloride (2 M.) is then added until the solution becomes pink; two drops of ferric chloride solution are then added whereupon a red-purple colour is produced if the test is positive and a yellow colour if negative. Reproducible determinations of acetic anhydride can be made using the ferric hydroxamate reaction.[74] Ketones can be detected and distinguished from saturated aliphatic aldehydes by oxidation with trifluoro-peroxo-acetic acid; only the former produce esters or lactones which can then be detected by the ferric hydroxamate test.[75] Another use of the ferric hydroxamate reaction is in an automatic colorimetric determination of penicillin.[76]

When carbonyl compounds react with hydroxylammonium chloride to form oximes an equivalent amount of hydrogen chloride is liberated:



$$>C = O + H_3\overset{+}{N}.OH.Cl^- \rightarrow >C = N.OH + HCl + H_2O$$

The determination of the amount of hydrochloric acid produced provides a method for the determination of the carbonyl content of the sample under examination. A modification of this method has been applied to the identification and characterization of ketones.[77] The carbonyl content of various celluloses has been determined by the oximation method; it was found possible to detect one carbonyl group in a cellulose molecule of 8400 glucose units.[78] The interference of peroxides in the determination of the carbonyl number with hydroxylamine can be eliminated by subtracting, from the carbonyl number found, the peroxide number multiplied by 5·6.[79] In connection with the determination of hydroxylamine in plant material, a critical review of the methods used for this determination has been published.[80, 81] The effect of light, pH, duration of reaction, interfering substances such as vitamin *C*, phenols and ketones was thoroughly investigated. Direct methods were rendered impracticable by interference and so a 'loss coefficient' was introduced; the determination was carried out with and without the addition of a known amount of hydroxylamine and from the values so found the coefficient was calculated. Hydroxylammonium formate in methyl alcohol is said to be a convenient reagent for the oxidation of carbonyl compounds.[82] Potentiometric titration curves with the reagent are said to have good inflexion points and good end-points are claimed if the excess of hydroxylamine is titrated with perchloric acid in dioxan, using thymol blue as the indicator. A method for the determination of aldehydes has been described, in which an excess of hydroxylammonium chloride is used, and the determination performed by the determination of the liberated hydrochloric acid with sodium hydroxide.[83] Acetaldehyde oxime yields a polarographic reduction wave which is said to be ideally suited for the amperometric titration of the aldehyde in aqueous solution; ethyl alcohol, ethyl acetate and acetic acid do not interfere.[84]

Hydroxylammonium chloride or sulphate produces a stable yellow colour with ammonium molybdate; the addition of aqueous germanic acid or neutralized sodium germanate and boiling changes the colour to apple-green or blue-green depending on the germanium concentration.[85] This test can be used to detect 0·4 μg. Ge in 0·05 ml. of solution; arsenate and phosphate do not interfere whereas oxidizing and reducing agents, and substances which precipitate molybdate, do interfere.

The addition of the dihydroxylammonium salt of dihydroxymaleic acid to a solution of titanium at pH 2·4 gives an intense colour, which can be used for the spectrophotometric determination of titanium at 400 mμ.[86]

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Hydroxylammonium sulphate, on a silica gel carrier, has been used in place of lead dioxide to absorb the oxides of nitrogen formed during the determination of carbon and hydrogen in nitrogen-containing compounds; nitric oxide, which is not absorbed, is oxidized to nitrogen dioxide, which is absorbed, by the oxygen occluding power of the silica gel itself.[87, 88] Amidosulphuric acid[89] and its ammonium salt[88] have also been used as replacements for lead dioxide in carbon–hydrogen determinations. Amidosulphuric acid has been used as a primary standard in non-aqueous titrations.[90]

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SECTION XXII

INDUSTRIAL ASPECTS OF THE OXIDES OF NITROGEN

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NOMENCLATURE

Mixtures of nitric oxide, nitrogen dioxide, dinitrogen tetroxide and dinitrogen trioxide frequently occur as intermediates in industrial chemical processes. These mixtures are commonly referred to as 'nitrous gases', indicating a relationship to nitrous acid. They do not, however, contain nitrous oxide, which has properties very different from those of the other oxides of nitrogen, and the name is in many ways unfortunate. In the nomenclature of the individual oxides there is an inexcusable laxity, particularly with reference to the extremely important distinction between nitric oxide and nitrous oxide. For example 'nitric oxide' has been suggested as a suitable medium for use in the manufacture of whipped cream when, presumably, nitrous oxide was meant. Again the present-day usage of the term nitrogen peroxide is incorrect in view of the absence of a peroxy-linkage in any of the molecular species involved. The names currently adopted in English scientific papers are given below after the formula. (The question of nomenclature will be discussed later, p. 189.)

N_2O	nitrous oxide
NO	nitric oxide
N_2O_3	dinitrogen trioxide
N_2O_4	dinitrogen tetroxide
NO_2	nitrogen dioxide
N_2O_5	dinitrogen pentoxide

INDUSTRIAL PREPARATION OF THE OXIDES

Nitrous Oxide

Nitrous oxide is the only oxide of nitrogen manufactured in Great Britain. The manufacture of nitrous oxide is carried out industrially by an extension of one of the laboratory processes, whereby ammonium nitrate is thermally decomposed. Apart from considerations of actual plant, the main purpose of the various patents taken out on this process has been the elimination of the hazard of an explosion, since, as is well known, ammonium nitrate is a high explosive, although it is difficult to detonate. The use of solid ammonium nitrate with a catalyst such as a solid compound of phosphorus, arsenic, molybdenum, silver or manganese has been suggested.[1, 2] More recent patents have been concerned with the use of aqueous solutions (approximately 80% by weight of ammonium nitrate) which are led into a reaction vessel held at about 275° where a layer of molten anhydrous ammonium nitrate forms above the inlet point. In this way nitrous oxide of high purity is said to be produced.[3, 4] The continuous agitation caused by the feed of aqueous solution, coupled with the absence of any stirrer lubricants, reduces the danger of explosion.

The industrial production of nitrous oxide by reaction between hydroxylamine and a nitrite in aqueous solution has been suggested,[5] but a more attractive method appears to be the controlled oxidation of ammonia. The oxidation of ammonia by oxygen in the presence of a catalyst yields a variety of products in various amounts, depending on the experimental conditions. The actual mechanism of the process has not been elucidated to the satisfaction of the various investigators and recent notes by Krauss[6] and Andrussov[7] do not appear to have clarified the matter. On the basis of numerous experiments Bodenstein[8] suggested the following reactions:

$$NH_3 + O \rightarrow NH_3O$$

For the formation of nitric oxide:

$$\begin{aligned} &NH_3O + O_2 \rightarrow HNO_2 + H_2O \\ &HNO_2 + O_2 \rightarrow HNO_4 \\ &HNO_4 \rightarrow NO + O_2 + OH \\ &2OH \rightarrow H_2O + O \end{aligned}$$

For the formation of nitrous oxide:

$$\begin{aligned} &NH_3O + O \rightarrow HNO + H_2O \\ &2HNO \rightarrow H_2O + N_2O \end{aligned}$$

For the formation of nitrogen:

$$\begin{aligned} &HNO_2 + NH_3 \rightarrow 2H_2O + N_2 \\ &HNO + NH_3O \rightarrow 2H_2O + N_2 \end{aligned}$$

together with the decomposition of nitric oxide and nitrous oxide.

The scheme given by Krauss[9] is similar to Bodenstein's except for the introduction of a reaction previously disregarded[10, 11]:

$$NH_3 + NH_3O \rightarrow N_2 + H_2O + 2H_2$$

and the reaction:

$$NH_3O + HNO_2 \rightarrow N_2O + 2H_2O$$

with omission of the species HNO_4.

This scheme has been criticized, however, on the ground that the reaction:

$$NH_{3\,\text{ads.}} + O_{\text{ads.}} \rightarrow NH_3O_{\text{ads.}}$$

is endothermic[12] (writing NH_3O as hydroxylamine).[13] Similarly it has been stated that the reaction of ammonia with certain oxides is appreciably endothermic. Zawadzki[12] considers that very nearly every impact of an ammonia molecule with the catalyst surface is effective and therefore that an endothermic reaction cannot be the first step. The alternative scheme is given below:

$$NH_3 + O \rightarrow NH + H_2O$$

For the formation of nitric oxide:

$$\begin{aligned} &NH + O_2 \rightarrow HNO_2 \\ &HNO_2 \rightarrow NO + OH \\ &2OH \rightarrow H_2O + O \\ \text{or}\quad &2HNO_2 \rightarrow NO + NO_2 + H_2O \end{aligned}$$

or Bodenstein's reactions involving HNO_4.

For the formation of nitrous oxide:

$$\begin{aligned} &NH + O \rightarrow HNO \\ &2HNO \rightarrow N_2O + H_2O \end{aligned}$$

For the formation of nitrogen:

$$\begin{aligned} &NH + NH \rightarrow N_2 + H_2 \\ &NH + NH_3 \rightarrow N_2H_4 \text{ (decomposition)} \\ &NH_3 + HNO_2 \rightarrow N_2 + 2H_2O \\ &2NO \rightarrow N_2 + O_2 \\ &2N_2O \rightarrow 2N_2 + O_2 \end{aligned}$$

The only other mechanism to be mentioned here is that of Andrussov, who proposes as a primary step the reaction between molecular oxygen and ammonia.[14]

$$NH_3 + O_2 \rightarrow HNO + H_2O$$

This has been criticized on the basis of considerations of the nature of oxygen on the surface of platinum, particularly with respect to the necessity for assuming the presence of activated oxygen molecules.

It has been pointed out that although the catalytic oxidation of ammonia for the preparation of nitrous oxide was patented in 1928–1930[15, 16, 17] very little has since been done to extend or verify this work.[18] The oxidation of ammonia on rhodium, palladium and iridium catalysts was studied in 1928.[19] Later it was found that, using manganese catalysts containing iron or bismuth at 200–300°, it was possible to obtain an 81–88% yield of nitrous oxide.[20] More recent work[18] using manganese oxide–bismuth oxide catalysts at 200° yielded 71% of nitrous oxide, with an initial gas composed of about 10% of ammonia and 90% of oxygen, but the efficiency of the catalyst decreased rapidly after about 40 hr. It appears that the formation of nitrous oxide is favoured by low temperatures and low rates of gas flow.[21, 22] The use of various catalysts has been described[23, 24] and the practical aspects of the kinetics of the process, together with its mechanism, have been discussed.[25] An interesting paper describes the low temperature catalytic oxidation of ammonia using either fused salts or a porous alundum tube impregnated with either a rare earth oxide or a mixture of manganese oxide and bismuth oxide. It is suggested that oxides which are semi-conductors of the *P*-type (lacking some electrons) are more active than those of the *N*-type (having available electrons).[26]

A thermodynamic study has been reported dealing with the ammonia oxidation reactions where the products may be nitrogen, nitric oxide, nitrous oxide or nitric acid.[27]

Nitric Oxide

Because of its importance in the manufacture of nitric acid, the oxidation of ammonia to nitric oxide has been the subject of many patents. It has been suggested that the best catalyst for the reaction:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

is Co_3O_4, and that the maximum efficiency is attained with 11% of ammonia in the air–ammonia mixture.[28] The catalyst loses none of its activity if the operating temperature is kept below 830°.[29] The influence of the walls of the containing vessel on this reaction has been discussed.[30] It has been suggested that the fact that the optimum temperature and contact time for the production of nitric oxide depend on the dimensions of the vessel is to be attributed to the decomposition of part of the ammonia prior to contact with the catalyst.[31] It has been reported that in order to obtain high yields of nitric oxide the catalyst must be capable of activating oxygen and dehydrogenating HNO.[32] The oxidation of ammonia in the presence of water vapour has also been examined.[33]

Many of the patents filed are concerned with the nature of the catalyst. Among those mentioned are a platinum alloy containing 2–5% of rhodium,[34] platinum screens which have been subjected to some mechanical treatment,[35] rhodium mixed with other metals of the platinum group,[36] a platinum alloy covered with a solid surface coating of pure platinum,[37] a mesh consisting of at least three different wires, one being of platinum and the other two of an alloy of platinum,[38] and a platinum–rhodium screen containing 1–25% of rhodium and 0.01–0.5% of a refractory oxide.[39]

Because it lacks industrial interest, the oxidation of ammonia in the absence of a catalyst has received little attention. It has been suggested that the mechanism of the reaction is the dehydrogenation of ammonia followed by the oxidation of the hydrogen thus produced.[40] Experimental results indicate that there is a sharp increase in reaction rate as the percentage of oxygen in the original mixture is increased.[41, 42] As a mechanism for the process the following steps were proposed:

$$NH_3 \rightarrow NH + H_2$$
$$NH + O_2 \rightarrow NO + OH \quad (\text{or } HNO_2)$$

Oxides of Nitrogen

Numerous methods have been suggested for the industrial preparation of the oxides of nitrogen, particularly by the reduction of nitric acid. The publications between 1933 and 1941 relating to the production of nitric oxides have been comprehensively reviewed by Waeser.[43, 44] The preparation of concentrated oxides of nitrogen by reducing mixtures of nitrous gases and water vapour with gases rich in hydrogen on a catalyst such as platinum, certain oxides or zeolites, for example, has been suggested.[45] Alternatively solutions of nitrites may be caused to react with nitric acid to yield 'nitrous gases',[46] which are then treated in countercurrent with fresh incoming nitric acid,[47] preferably at elevated temperatures.[48] Several patents relate merely to the reaction between oxides of nitrogen and nitric acid to produce highly concentrated oxides of nitrogen.[49–51].

The use of sulphur dioxide[52] or carbon[53] as reducing agents has been suggested for the production of nitric oxide. For example by reducing nitric acid below 450° in the vapour phase, and using at least 1·5 mol. of sulphur dioxide per mol. of nitric acid, nearly pure nitric oxide is obtained.[54] By altering the conditions of reaction it is possible to obtain nitrogen dioxide as the main product.[55, 56] In one process the gaseous sulphur dioxide is passed into aqueous nitric acid containing not less than 40% HNO_3 at a temperature of 15–35°, and the reaction is stopped when half of the nitric acid originally present has reacted.[57]

Another important method suggested for the production of oxides of nitrogen is the decomposition or reaction of nitrosyl chloride. It is interesting that nitrous oxide is said to be produced by the reaction between nitrosyl chloride and carbon monoxide at high temperatures.[58] More recently it has been suggested that nitrosyl chloride be mixed with air or oxygen, followed by heat treatment at approximately 200–300°.[59, 60] It has also been said that the reaction may be carried out at 50° at high pressures,[61] or by heating the nitrosyl chloride to its dissociation temperature (700°) and cooling rapidly in air.[62] Another reagent for the oxidation of nitrosyl chloride is nitric acid.[63] The general principle in this reaction is the passage of the nitrosyl chloride through a hot nitric acid solution containing about 70% of HNO_3.[64, 65] A similar technique is to pass nitrosyl chloride over nitrates heated to about 300°, whereby a gas containing only traces of chlorine is obtained.[66] Metallic iron,[67] or heated oxides, hydroxides or carbonates,[68] have been used for the same purpose. Yet another method depends on reaction between nitrosyl chloride and hydrogen, at 400° or in the presence of a catalyst, whereby hydrogen chloride and nitric oxide are obtained.[69, 70]

Miscellaneous methods include the catalytic oxidation of cyanogen on platinum gauze so that more than 90% of the cyanogen is oxidized to nitric oxide, [71] the maximum yield being obtained at 700°–800°. The continuous production of nitrogen dioxide by the pyrolysis of calcium nitrate mixed with sand has been studied,[72] and the catalytic oxidation of ammonium salts with nitrogen dioxide has been suggested as a method for producing lower oxides of nitrogen.[73] The purity of compressed nitric oxide and nitrogen dioxide may exceed 99% and 98% respectively.[73a]

The preparation of dinitrogen pentoxide is not of industrial interest, and there are very few patents on the subject. The main reaction is essentially that commonly used for the laboratory preparation, viz., the reaction of a lower oxide of nitrogen, other than nitrous oxide, with ozone,[74, 75, 76] the reactants being mixed as two gaseous currents, preferably at a temperature below −20°. More recently a novel method has been developed in which a solution of nitrogen dioxide in concentrated nitric acid is electrolysed at −25° using a platinum anode.[77] The reaction proceeds according to the scheme:

$$2NO_3^- + N_2O_4 \rightarrow 2N_2O_5 + 2e$$

REACTIONS OF INDUSTRIAL INTEREST

The properties of the oxides of nitrogen have been reviewed,[78] as have their explosive reactions with combustible gases.[79] Miscellaneous reactions include the addition of nitric oxide and nitrogen dioxide to the gases generated when phosphorus is sublimed in an electric furnace, to remove phosphorus and phosphine[80]; the decomposition of certain natural phosphates by a mixture of sulphur dioxide and nitrogen oxides, to obtain material suitable for the preparation of fertilizers[81]; and the etching of metals.[82] It has been reported that it is possible to dye certain woods by treatment, for example, with gaseous oxides of nitrogen,[83] and that the treatment of coal with nitrous oxide, nitrogen dioxide or nitric oxide at approximately 300° produces a fuel having reduced smoke yield, caking ability and swelling power.[84] The corrosion of iron containing small amounts of carbides, oxides and sulphides by gaseous nitrogen oxides has been discussed.[85] The effect of nitrogen dioxide on metals is discussed more fully in a later section.

One of the most important reactions from an industrial point of view is the effect of nitrogen oxides on dyes present on acetate rayon fabrics. This so-called 'gas fading' has been shown to be due primarily to 'nitrous gases'.[86] Nitrogen oxides are normally present in the atmosphere to the extent of about 0·003 p.p.m., but in a smoky atmosphere their concentration may rise to about 0·15 p.p.m.[87] It has been suggested that some of the acetate groups are replaced by nitro groups, whilst in the dyestuff there is diazotization of the free amino groups. Although, as is to be expected, nitrous oxide has no effect, it has been noted that spectroscopically pure nitric oxide produces an effect very similar to that observed with gas fading.[88] The use of gases obtained by the combustion of illuminating gas has been suggested for the study of gas fading,[89, 90, 91] and various accelerated gas fading tests have been described.[92, 93]

The Reaction $2NO + O_2 \rightleftharpoons 2NO_2$

The oxidation of nitric oxide with oxygen is familiar as one of the classical termolecular reactions. It is of considerable importance industrially since many of the methods for removing oxides of nitrogen are to a certain extent controlled by the velocity of this reaction.

It is interesting that all the well-known third-order reactions in the gaseous phase involve the participation of nitric oxide. The suggestion that one of the reacting species is NOX or N_2O_2 is, therefore, not unexpected. The account of this reaction given below is primarily chronological.

Classical work on the oxidation of nitric oxide by oxygen was carried out by Bodenstein and co-workers, the first paper appearing in 1918.[94] Here it was shown that the reaction is of the third order in the temperature range studied (0–90°) so that the rate of reaction may be written $dx/dt = k[O_2][NO]^2$. A further interesting point about this reaction is that the rate falls with increasing temperature. This research was subsequently extended to the temperature interval 140–390°,[95] pressures being measured with a bromonaphthalene manometer.

It is clear that, whereas for many bimolecular reactions occurring at a reasonable rate only about one collision in 10^{11} is effective, termolecular collisions are so rare that unless the energy of activation is extremely small the reaction rate will be negligible. For simple termolecular reactions a very small heat of activation is therefore to be expected. Bodenstein suggests that the relative frequencies of ternary and binary collisions are approximately in the ratio of a molecular diameter to the mean free path. In a normal gas at about N.T.P. this gives a ratio of 1:1000 and allowing for an orientation effect this leads to an activation energy in the region of a few kcal. This of course does not immediately account for the inversion of the temperature effect which is in fact observed. The reaction has been extensively studied, but appears to be third-order over a wide range of experimental conditions,[96-104] the results generally being in accord with those of Bodenstein. The results of several of Bodenstein's investigations have been summarized,[105] and Table I contains data taken from his original papers.[95] The values of k are in mole^{-2} 1.^{2} min^{-1}.

Table I.—The Effect of Temperature on the Rate Constant for the Reaction $2NO + O_2 \rightarrow 2NO_2$

T°K.	$k_c \times 10^{-6}$ (mole/l.)$^{-2}$ min.$^{-1}$
273	2·09
363	1·08
470	0·80
564	0·68
662	0·61

As Bodenstein points out, the equilibrium:

$$2NO_2 \rightleftharpoons N_2O_4$$

is reached rapidly and causes only technical difficulties, not important to an understanding of the kinetics. Essentially the postulated reaction mechanism is[106]:

$$\begin{aligned} 2NO &\rightleftharpoons N_2O_2 \quad \text{(fast)} \\ O_2 + N_2O_2 &\rightarrow 2NO_2 \\ 2NO_2 &\rightleftharpoons N_2O_4 \quad \text{(fast)} \end{aligned}$$

The temperature coefficient may be written as the relative increase in velocity for 10° rise in temperature, k_{t+10}/k_t, and changes gradually from 0·912 to 0·997 as the temperature rises. Considering the common two-fold increase for 10° rise in temperature, it is clear that the energy of activation is indeed very low.[107]

More recently Daniels and Treacy[104] have suggested the following reaction mechanism:

$$\begin{aligned} &NO + O_2 \rightleftharpoons NO_3 \\ &NO_3 + NO \rightleftharpoons NO_3.NO \\ &NO_3.NO + NO_2 \rightarrow 2NO + O_2 + NO_2 \\ &NO_3 + NO_2 \rightleftharpoons N_2O_5 \\ &NO_3 + NO \rightarrow 2NO_2 \\ &NO_3.NO + NO \rightarrow 2NO_2 + NO \end{aligned}$$

These authors found that the use of the nitric oxide dimer did not enable them to develop suitable equations to account for the experimental behaviour, and remark that the species NO_3 (nitrogen trioxide) has been spectroscopically identified.[108] The evidence for the nitric oxide dimer will be discussed subsequently. It appears that the classical viewpoint of the reaction as termolecular is an oversimplification, but is nevertheless useful except at low pressures. It is of interest that the model of a reasonable transition state is quite close to a pernitrite (ONOO)–nitric oxide complex.[109] The formation of dinitrogen pentoxide (e.g. 20%) during the oxidation of nitric oxide by oxygen has been reported from infra-red evidence.[110] Ogg[111] favours the reaction scheme:

$$\begin{aligned} &NO_2 + O_2 + NO \rightarrow NO_3 + NO_2 \\ &NO_3 + NO_2 \rightarrow N_2O_5 \\ &NO_3 + NO \rightarrow 2NO_2 \end{aligned}$$

In a recent paper with Ray[111] the nitrogen dioxide catalysed oxidation of nitric oxide was studied; a rate constant of $6{\cdot}58 \times 10^7$ c.c.^{2} mol.$^{-2}$ sec^{-1} was obtained for the reaction:

$$NO + O_2 + NO_2 \rightarrow NO_2 + NO_3$$

at 25°.

The existence and significance of molecular complexes have been discussed. It appears to be possible to interpret the negative temperature coefficient in terms of a clustering caused by van der Waals forces,[112] and it has been pointed out that a reaction having a rate dependent only on the formation of a transitory activated complex, in which classical degrees of freedom are frozen out, must have a positive energy of activation.[113] The formation of dinitrogen trioxide as an intermediate oxidation product has not been accepted,[114, 115] and in recent years only the reactive dimer, N_2O_2, and NO_3[116-119] have been considered. The oxidation of nitric oxide has also been discussed on the basis of the Wigner spin conservancy rule,[130] where the multiplicity of the potential energy surface cannot change during a chemical reaction. The ground state of nitric oxide is a doublet, whilst that of most other molecules is either singlet or triplet. However the interaction of two doublets forms a singlet, favouring a reaction involving 2NO.

Apart from deviations from termolecular behaviour, there are considerable discrepancies in the literature concerning the homogeneous nature of this reaction. For example, at low pressures adsorption and surface effects appear to affect the rate,[121] the results suggesting that adsorbed nitric oxide introduces complications. By far the most striking observations, however, are those of Stoddart,[122] who in a series of careful experiments found that dry nitric oxide and oxygen do not react if the mixing occurs in the dry oxygen bulb. A bulb containing nitric oxide and oxygen was colourless, but on heating in boiling water became brown. Since this is a direct visual observation, it becomes extremely difficult to regard the reaction as homogeneous. Stoddart considers that the $(NO)_2$ dimer is formed on the walls of the vessel but reacts homogeneously. Although water has been reported to affect the rate of this reaction,[123, 124] so that the reaction takes place more slowly with dry materials,[125] Stoddart's observations have not been confirmed.[126]

Various investigators have reported that the kinetics of the oxidation of nitric oxide are best explained in terms of a reaction that is at least in part heterogeneous,[99, 127-132] whilst studies of the reaction carried out in flow systems appear to indicate that the surface effect is greater for mixtures low in oxygen.[132] In view of the great technical importance of this reaction, the effect of catalysts has been extensively studied. In 1929 it was observed that highly sorptive forms of carbon may increase the reaction rate as much as 500 times.[133] It has been reported that glass wool has no effect,[134] in contrast to the catalysis reported above,[99] but silica gel was found to produce a considerable effect. The catalytic activity of silica gel has been extensively studied and is commercially important,[135-139] whilst zeolitic catalysts have also been used.[140] The use of activated carbon has been extended[141-143] and miscellaneous substances which have been studied as possible catalysts include mercury,[144, 145] pumice,[146] cobalt oxide[147] and chromium and zinc alloys.[137]

Kornfeld initially supposed that a magnetic field slightly accelerated the reaction between nitric oxide and oxygen,[148] but subsequently changed her mind.[149] In the 1920s there was some interest in the possibility of the formation of gaseous ions during reactions, and the oxidation of nitric oxide was studied from this point of view.[150-152] The mechanism of the oxidation of nitric oxide in various discharges has also been examined.[153-155]

Although it has been said that the reaction between ozonized oxygen and nitric oxide is an example of catalysis by ozone,[156] subsequent studies have shown that the reaction is an elementary bimolecular process[157, 158]

$$NO + O_3 \rightarrow NO_2 + O_2$$

as originally proposed by Briner *et al.*[159] Nitric oxide and ozone explode violently at liquid-air temperatures.[160] Oxygen atoms react with nitric oxide at −183°.[161] The reaction:

$$NO + O \rightarrow NO_2 + h\nu$$

has been used as a means of measuring the concentration of atomic oxygen in flames.[162]

The Reaction $NO_2 \rightarrow NO + \frac{1}{2}O_2$

has not been extensively studied from the thermal aspect although the photochemical decomposition has been fully examined. Giauque and Kemp have given an excellent summary of work on the thermal reaction.[163] Bodenstein[95] reports that the velocity of the decomposition of nitrogen dioxide is given by the expression:

$$dx/dt = k'[NO_2]^2 - k[NO]^2[O_2]$$

The velocity constant k' increases with temperature and in the range 319–383° the increase is 1·5 fold per 10° rise in temperature. This gives a critical increment of 32 kcal. mole^{-1} which compares favourably with that calculated by Hinshelwood's method (33·2 kcal. mole^{-1}).[164]

At sufficiently low partial pressures it has been shown that in the photochemical decomposition of nitrogen dioxide the recombination of nitric oxide and oxygen is so slow that it may be neglected, enabling quantum yield determinations to be made.[165] The quantum efficiency has been examined as a function of wave-length,[166] and the photochemical threshold (which is in the middle of the nitrogen dioxide absorption region[164]) has been found to be sharper than was originally supposed, light of $\lambda = 436$ mμ being ineffective, whilst that of 405 mμ has a quantum efficiency given by $\gamma = 0{\cdot}74$.[167] The mechanism given by Norrish is:

$$NO_2 + h\nu \rightarrow NO_2'$$

$$NO_2 + NO_2' \rightarrow 2NO + O_2$$

Alternatively it has been postulated that the primary process involves dinitrogen tetroxide,[168]

$$N_2O_4 + h\nu \rightarrow 2NO + O_2$$

However the Norrish mechanism has been confirmed and it has been shown that dinitrogen pentoxide does not affect the efficiency of the process.[169]

More recently Norrish and Porter[170] have examined the decomposition by the flash photolysis technique. With a gas volume of about 500 c.c. and one flash of 4000 joules the nitrogen dioxide at 4 cm. pressure of mercury was nearly completely decomposed. This observation has been further discussed.[171] The decomposition of nitrogen dioxide in an electric discharge[172, 173] and also under neutron irradiation[174] has been studied.

The Equilibrium $2NO_2 \rightleftharpoons 2NO + O_2$

has also been studied by Bodenstein,[95] between 220° and 550°; the equilibrium constant is given by the expression:

$$\log K_p = (-5749/T) + 1{\cdot}70 \log T - 0{\cdot}00050T + 2{\cdot}839$$

p being measured in atmospheres. Giauque and Kemp[163] have discussed the equilibrium fully and suggest that for the reaction: $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ $\Delta G^\circ_{298{\cdot}1} = -8375$ g.-cal. and $\Delta H^\circ_{298{\cdot}1} = -13{,}562$ g.-cal.

These values may be compared with the spectroscopic data of Zeise.[175]

THE REMOVAL OF OXIDES OF NITROGEN FROM INDUSTRIAL GASES

Although nitrogen dioxide, for example, may sometimes be partially removed simply by allowing it to condense at normal temperatures, in many instances the concentration of the oxides is too low to permit this procedure. One suggestion to facilitate condensation is the addition of small quantities of nitric acid,[176] coupled with an increase in pressure if this is necessary,[177] but this again is possible only for relatively high concentrations of nitrogen dioxide. The method of removal in other cases depends to a certain extent on whether the aim of the process is removal of the oxides from a stream of otherwise useful gas (e.g., to avoid corrosion problems) or the recovery of the nitrogen oxides for subsequent use (e.g., in the production of nitric acid). The two problems are, however, related in that an efficient means of removal is frequently valuable also for recovery.

A problem on which much work has been done is frequently referred to as the 'gum' problem. Gum formation appears[178] to be due to the reaction between nitric oxide, for example, and conjugated olefines such as butadiene and *cyclo*pentadiene, which may occur in towns gas. Most of the gum formation occurs in the gas holders, settling being rapid where condensation also occurs. Numerous papers[179–187] deal with the removal of gums, the formation of gums and means of avoiding their initial formation. The problem of nitrogen dioxide in coke-oven gas has been reviewed,[188] as also has the complete purification of fuel gas.[189]

Some attention has been given to the removal of oxides of nitrogen from gases by electrical means. For example a high-tension electric field has been used in conjunction with an iron filter sprayed with sulphuric acid.[190] Gas treaters involving brush-type corona discharges have been described,[191–193] as has the removal of nitrogen oxides by an electrical tar precipitator.[194]

Iron oxides,[195–198] iron sulphides[199–202] or chromous compounds[203] have been used to remove nitric oxide from gases. The use of various catalysts has been suggested to accelerate reduction of the nitric oxide content of gases containing hydrogen, the treated gas containing only one or two p.p.m. of nitric oxide.[204–207] Alternatively the use of lower oxides of sulphur, or salts such as sulphites, has been proposed.[208–210] Other methods involve bringing the gas into contact with the anode of an electrolytic cell at which oxygen is being evolved,[211] treatment with sulphides of molybdenum or tungsten[212] or ammonium bicarbonate[213–215] and treatment with gaseous sulphur trioxide to yield a solid compound that can be filtered out of the gas stream.[216] Calcium carbonate and calcium oxide have also been used to remove nitrous vapours.[217–220]

Adsorption processes whereby the gases may subsequently be obtained in a more concentrated form have been much studied.[221–225] It has been suggested that activated carbon is a better adsorbent than silica gel and should preferably be cooled to 10–12° during use.[226] The carbon is reported to be unchanged after the desorption process, but it has been suggested that appreciable quantities of carbon dioxide are formed during desorption by water vapour at 120–150°, the best method of regeneration being in vacuo at 600°.[227] More efficient initial adsorption is of course secured at higher pressures of the order of 10 atm.[228] Adsorption by alumina gel converts the nitric oxide into nitrogen dioxide if air is present in excess, and the importance of working at a low temperature is again stressed.[229]

Silica gel has recently found favour as an adsorbent for nitric oxide, nitrogen dioxide being produced in the presence of oxygen.[230] The present treatment of gases containing small quantities of nitric oxide is to cool to remove water and then oxidize catalytically on a silica gel bed, yielding nitrogen dioxide which is removed by cooling to −18°.[231–234] Ogg[235] has suggested alternatively the use of an absorbent mass prepared by heating a mixture of sodium nitrate and iron oxide, while absorption of nitric oxide in an aqueous solution of a hexavalent chromium compound has also been proposed.[236]

THE SOLUTION OF OXIDES OF NITROGEN IN SULPHURIC ACID (NITROSES)

Nitrous oxide and nitric oxide apparently do not react with concentrated sulphuric acid. The other oxides are soluble and yield nitronium and/or nitrosonium

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ions. These reactions, which are well understood and have been fully investigated by cryoscopic techniques,[237, 238] may be written:

$$N_2O_5 + 3H_2SO_4 \rightarrow 2NO_2^+ + H_3O^+ + 3HSO_4^-$$
$$N_2O_4 + 3H_2SO_4 \rightarrow NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$
$$N_2O_3 + 3H_2SO_4 \rightarrow 2NO^+ + H_3O^+ + 3HSO_4^-$$

The van't Hoff i factor in each case is approximately 5·7. The conversions are quantitative except for the partial recombination of the ions of the semi-strong base, water. Clearly dilution of the sulphuric acid will affect the above reactions. From the industrial viewpoint the systems are therefore more complex, although the fundamental principles are the same. It is rather interesting that in 1921 Sanfourche[239] discussed the reaction of a mixture of nitric oxide and nitrogen dioxide with sulphuric acid in terms of the equations:

$$NO + NO_2 \rightleftharpoons N_2O_3$$
$$N_2O_3 + 2H_2SO_4 = 2HNOSO_4 + H_2O$$

which are strikingly similar to the reactions given above.

The absorption of nitrogen oxides by sulphuric acid has been reported as a process the rate of which is determined by the diffusion in the gaseous and in the liquid phase and particularly by the viscosity of the liquid.[240] It has been suggested that dinitrogen trioxide is absorbed more readily in fairly concentrated acid, whilst nitrogen dioxide is absorbed more rapidly by dilute acid.[241] Kinetic studies are said to show that absorption of nitrogen dioxide is minimal at 80% by weight of sulphuric acid, and this is attributed to the high viscosity of this acid.[242] An excess of nitric oxide over that required for the formation of dinitrogen trioxide has been variously reported as lowering the absorption velocity,[243] having no effect,[244, 245] or producing some effect.[246] It has also been stated that a dinitrogen trioxide mixture is absorbed more rapidly than nitrogen dioxide in concentrated acid.[247] The absorption process has recently been fully discussed.[248, 249]

Work on the vapour pressure of water vapour and oxides of nitrogen over their solutions in sulphuric acid has been reported, mainly by Russian investigators. The discrepancies existing among the data of various investigators have been noted, and from experimental data on various preparations of nitrosyl bisulphate in sulphuric acid it is deduced that the probable reason for these differences is the occasional presence of nitric acid in certain preparations, or the use of unreliable analytical techniques.[250] Several investigators have studied this problem and numerous empirical equations or nomograms have been proposed.[251-261] The heat of solution of nitrogen oxides in sulphuric acid has been examined,[261-264] as also has the relationship between the specific gravity of the solutions and their nitrogen oxide content.[265] The solubility of nitric oxide in a nitrosyl bisulphate solution in sulphuric acid has been measured,[266] and also the rate of desorption of oxides of nitrogen.[267]

The conductivity of solutions of nitrogen dioxide in sulphuric acid has been studied.[268]

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SECTION XXIII

THE FIXATION OF NITROGEN VIA THE OXIDES

BY I. R. BEATTIE

General Survey

'The consumption of nitrogenous matters in the cultivation of lands cannot be made good by the nitrogen compounds formed by natural processes.' This statement was made some thirty years ago by Mellor (VIII, 365) and is still true today. To overcome this deficiency enormous changes have occurred in the nitrogen fixation industry since that time. For example, there was practically no synthetic ammonia produced in the United States of America in 1920, whereas the production there in 1950 was of the order of 1,700,000 tons. It is worth remarking, too, that over a farm of about 160 acres there is the same quantity of nitrogen available as was fixed in the whole world during 1950 (that is about 4,500,000 tons).[1]

Although it is not always fully realized, there is at present only one synthetic process of industrial importance for the fixation of nitrogen. This is the well-known Haber process involving the direct combination of nitrogen and hydrogen in the presence of a suitable catalyst. The catalyst is frequently prepared by passing hydrogen and nitrogen over an intimate mixture of iron oxides, alumina and potassium carbonate at a high temperature (see Vol. VIII, Suppl. 1 page 259).

In comparison with other processes which have been suggested for nitrogen fixation, this method is perhaps best described as elegant, although pressures of up to 1000 atm. are used in conjunction with temperatures in the range 450° to 1000°, and the reactant gases must be very carefully purified.

The cyanamide process is used to a limited extent for nitrogen fixation. Here coke and lime are heated together in an electric furnace to yield, as the primary product, calcium carbide. This is then finely ground and treated with nitrogen in small cylindrical ovens at about 1000°, with the relatively slow formation of calcium cyanamide, $CaCN_2$. The product is normally crushed, oiled to reduce its dustiness, and sold directly as fertilizer. It is toxic, and it has been suggested that this industry will eventually die out.[2]

The following reactions have been examined from the point of view of their value in the fixation of nitrogen[3, 33]:

$$N_2+O_2 = 2NO \tag{1}$$

$$N_2+2CO_2 = 2CO+2NO \tag{2}$$

$$N_2+2C+H_2 = 2HCN \tag{3}$$

$$N_2+C_2H_2 = 2HCN \tag{4}$$

$$N_2+2CH_4 = 2HCN+3H_2 \tag{5}$$

It was decided that reaction (1) was the only feasible method, although the raw materials for reaction (5) were cheap and the products of the side reaction $2CH_4 \rightleftharpoons C_2H_2+3H_2$, augmented by the by-product hydrogen, were valuable.

The arc process (whereby oxygen and nitrogen are caused to react in the zone of an electric discharge) is now obsolete, at least in its original form. Even in Norway where electricity is cheap, the Haber process was rapidly gaining ground as early as 1930. The available electrical power is now used for the electrolytic production of hydrogen for the Haber process. There is, however, still a considerable interest attached to the arc process, as is shown by the number of patents and research papers which continue to appear on this subject.

In the United States of America the combustion of air–gas mixtures to produce the temperatures, of the order of 2000°, necessary to obtain a reasonable amount of reaction between atmospheric oxygen and nitrogen, has also been studied and has reached the pilot plant stage.

The Fixation of Nitrogen by Natural Processes

Nitrogen fixation in nature occurs in two ways: by bacterial action and by electric discharge. Nitrogen-fixing bacteria are of two main kinds: those which live in the soil in a free state and those present in nodules on the roots of leguminous plants, such as peas and beans. These plants have an important effect in increasing the nitrogen content of any soils in which they grow. The mode of action of these bacteria is not yet known.

In a lightning discharge oxides of nitrogen are produced as in the arc process, and, owing to the presence of excess of oxygen, appear eventually as nitric acid of very low concentration in rain-water. The amount of combined nitrogen which reaches the earth's surface from this source is very large.

Nitrogenous compounds are found in coal, and in the destructive distillation of coal this nitrogen appears in various forms, one being ammonia. Ammonia so produced is frequently converted directly into ammonium sulphate for subsequent use as a fertilizer.

The natural deposits of nitrates, amongst them the famous Chile saltpetre beds, may be regarded as sources of naturally fixed nitrogen. The main deposits occur in Argentina, California, and to a greater extent in the rainless districts on the west coast of South America. They are still of considerable importance. (See Mellor, II, Supplement 2, p. 1206.)

The Reaction $N_2 + O_2 \rightleftharpoons 2NO$

The free energy change in the reaction between nitrogen and oxygen to produce nitric oxide is large and positive. (ΔG° is approximately 20 kcal. mole^{-1}.) It is clear therefore that to obtain a reasonable yield of nitric oxide (even at equilibrium) the temperature must be high. Further, the rate of cooling from the temperature of reaction must be high enough to ensure the 'freezing in' of the greater part of the nitric oxide present in the equilibrium mixture. Although the kinetics of the reaction between nitrogen and oxygen have not been extensively studied, owing largely to the experimental difficulties, much work has recently been done on the reverse reaction, the decomposition of nitric oxide.

The thermal decomposition of nitric oxide has been examined by many investigators, but in several cases their results are in direct conflict. This is perhaps not surprising in view of the fact that the reaction as normally studied is heterogeneous over part of the temperature range available for examination. The chief basis for discussion is found in the work of Kaufman and Kelso,[4] who have attempted to co-ordinate the previously conflicting experimental data. However, the present state of this study is not completely satisfactory and new experimental data will be necessary before the reaction can be said to be fully understood.

DECOMPOSITION OF NITRIC OXIDE UP TO 1330°

The rate of decomposition of 99·98% pure nitric oxide in silica vessels has been studied by Wise and Frech.[5] Their results indicate that the rate of decomposition of nitric oxide is of the second order over the temperature range 600° to 1000°, although the temperature coefficient for the specific rate constant varies with temperature. This is interpreted in terms of a low-temperature (up to 700°) heterogeneous process and a high-temperature homogeneous mechanism. The effect of increasing the ratio of surface area to volume by a factor of 2·3 was studied from 630° to 1000°, and a significant increase in reaction rate was found, particularly at higher concentrations of nitric oxide. The heterogeneous nature of the reaction was still apparent at the highest temperature of study, 1000°.

The rate equation suggested for the reaction $2NO \rightarrow N_2+O_2$ below 700° is:

$$k_1 = 1{\cdot}4\times10^4 \exp(-21{,}400/RT) \text{ c.c. mol.}^{-1} \text{ sec.}^{-1} \tag{6}$$

Using the data at 1000° it is possible to evaluate the high temperature reaction constant k_2 in the form:

$$k_2 = 3{\cdot}1\times10^{15} \exp(-82{,}000/RT) \text{ c.c. mol.}^{-1} \text{ sec.}^{-1} \tag{7}$$

According to this interpretation the reaction rate above about 1100° is given by equation (7), and the reaction here is essentially homogeneous. In subsequent work[6] equation (7) has been modified to read:

$$k_2 = 2{\cdot}2\times10^{14} \exp(-78{,}200/RT) \text{ c.c. mol.}^{-1} \text{ sec.}^{-1} \tag{8}$$

During this later investigation it was shown that the addition of nitrogen retarded the heterogeneous reaction owing to poisoning of the surface, while oxygen enhanced the rate of reaction in the region 700° to 880°. On the basis of their experimental data Wise and Frech suggest the following reaction scheme:

$$2NO \rightarrow N_2O+O \tag{9}$$

$$O+NO \rightarrow O_2+N \tag{10}$$

$$N+NO \rightarrow N_2+O \tag{11}$$

$$O+O+(M) \rightleftharpoons O_2+(M) \tag{12}$$

These results, both experimental and theoretical, have been challenged.[7] A catalytic effect at 880° was not confirmed, while reaction (10) was adversely criticized in view of the high value for the dissociation energy of nitrogen (225 kcal. mol.$^{-1}$). This criticism has been answered by the original workers,[8] partly on the basis that a catalytic effect had been found previously.

The most recent experimental work in this temperature region is that of Kaufman and Kelso,[4] who again worked with silica vessels. In view of the uncertainties which may attach to a flow system this examination was conducted under static conditions. From the experimental data on the decomposition of nitric oxide in the presence of nitrous oxide, these authors assumed that chain reactions of long chain-length did not occur. However a small catalytic effect for oxygen was found at temperatures higher than 1180°. Thus at 1150° with p_{O_2} between 100 and 200 mm. Hg, and with p_{NO} constant at 100 mm. Hg, no acceleration in the rate was observed. At 1200° with a similar nitric oxide pressure, and p_{O_2} in the range 0 to 400 mm. Hg, a small increase in the rate was found, proportional to the square root of the oxygen pressure and in agreement with the results of Vetter.[9] (It should be noted that, contrary to the statement in the abstract cited, no catalyst was present.) Vetter proposed the following reactions involving a chain mechanism:

$$O+NO \rightleftharpoons N+O_2 \tag{13}$$

$$N+NO \rightleftharpoons O+N_2 \tag{14}$$

$$O+NO \rightleftharpoons NO_2 \tag{15}$$

$$O+NO_2 \rightleftharpoons NO+O_2 \tag{16}$$

$$N+NO_2 \rightleftharpoons 2NO \tag{17}$$

The results on the catalytic effect of oxygen can be interpreted in terms of the equation:

$$-d[NO]/dt = k_2[NO]^2+k_c[NO][O_2]^{1/2} \tag{18}$$

(where k_c is the rate constant for the oxygen catalysis) providing it is appreciated that the homogeneous reaction is rate controlling above 1130°. Below this temperature there is a region where heterogeneity becomes increasingly important.

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Kaufman and Kelso[4] plot Vetter's results at high $[NO]/[O_2]$ ratios[9] alongside their own experimental results on the decomposition, and also those of other workers. This is shown in Fig. 1, and it can be seen that the agreement is reasonable.

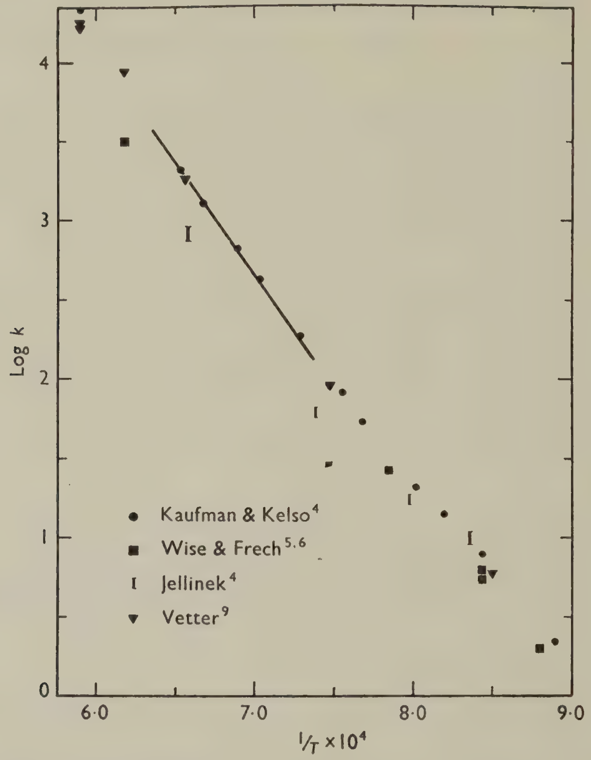

Fig. 1.—Temperature dependence of the thermal decomposition of nitric oxide

However, this apparent similarity between the results of Vetter and those of Kaufman and Kelso must be treated with caution as the latter results clearly apply to $[NO]/[O_2] \rightarrow \infty$. Summarizing the experimental data it is apparent that at higher temperatures, between about 1130° and 1330°, the reaction is of second order.

DECOMPOSITION OF NITRIC OXIDE AT ABOUT 2000°

The decomposition of nitric oxide has also been examined at temperatures between 1930° and 2130°[10] and the results have been discussed in comparison with those of Zeldovich[11] on the reaction between oxygen and nitrogen in flames. Zeldovich[11] carried out a non-isothermal study of the nitrogen–oxygen reaction at 1730° to 2630° and postulated the following reactions:

$$O + NO \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} N + O_2 \tag{19}$$

$$N + NO \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} N_2 + O \tag{20}$$

Supposing that oxygen molecules and oxygen atoms were in equilibrium he showed that:

$$\frac{[O_2]^{1/2}d[1/NO]}{dt} = \frac{2Kk_{+2}\{1-[NO_{eq}]^2/[NO]^2\}}{1+k_{+2}[NO]/k_{-1}[O_2]} \tag{21}$$

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where $K = k_{+1}[O]/k_{-1}[O_2]^{1/2}$, which is equal to the equilibrium constant of the reaction:

(22) $$NO = N + \tfrac{1}{2}O_2$$

Since the ratio $[NO]/[O_2]$ was usually small the denominator of the expression (21) was put equal to unity to yield a value for

$$2Kk_{+2} = 5 \times 10^{11} \exp(-86{,}000/RT)\ (\text{mole/l.})^{-1/2}\ \text{sec.}^{-1}$$

Since $[O_2]^{1/2}d[1/NO]/dt$ was not found to decrease with increasing $[NO]/[O_2]$, it is to be presumed that reaction (20) alone was measured, if the mechanism is correct. Fennimore and Jones studied the reaction in flat flames of nitrous oxide premixed with either hydrogen or carbon monoxide.[10] They also found that over a wide range of $[NO]/[O_2]$ ratios the value of $[O_2]^{1/2}d[1/NO]/dt$ remained constant, which would require an incredibly high value for k_{-1}. If the denominator of (21) is equal to unity, then their results are in agreement with this equation. They therefore suggest that nitrogen atoms are always in equilibrium with nitric oxide and oxygen, the measured reaction being in fact (20). Their data in terms of the mechanism of Zeldovich yield $2Kk_{+2} = 2 \times 10^{12} \exp(-98{,}000/RT)\ (\text{mole/l.})^{-1/2}\ \text{sec.}^{-1}$

Summarizing this information, it may be said that the experimental data between 1130° and 1330° are in agreement with a purely second order homogeneous reaction, whilst at high temperatures reactions involving atomic nitrogen and nitric oxide become important.

The heterogeneous decomposition of nitric oxide has been studied[12, 13, 14] and at first, on the surface of a platinum wire, it appeared to be unimolecular with respect to nitric oxide, uninfluenced by nitrogen but retarded by oxygen.[15] It was suggested that the reaction was bimolecular in the gas phase. Experimental work initially was essentially in agreement with this,[16] although it was subsequently observed[17] that retardation is serious enough to reduce the order from two to one. The decomposition of nitric oxide on platinum and platinum–rhodium (10%) wires above 1000° is bimolecular with respect to nitric oxide and retarded proportionally to the oxygen concentration. It has been predicted that the heat of adsorption of nitric oxide on platinum should be large and positive.[17] These results have been borne out by later workers.[18, 19] The effect of metallic oxides in decomposing nitric oxide has also been studied.[16, 20]

The photochemical decomposition of nitric oxide has been examined, although the results are not conclusive.[21] It has been suggested[22] that the decomposition occurs in agreement with the following reactions:

(23) $$2NO \rightarrow N_2 + O_2 \qquad 90\%$$

(24) $$3NO \rightarrow N_2O + NO_2 \qquad 10\%$$

More recently nitrogen and oxygen have been proposed as the only products.[23] In the case of the mercury-sensitized photo-decomposition the reaction may be written[24]:

(25) $$6NO \rightarrow N_2 + 2N_2O_3$$

A possible mechanism is:

(26) $$Hg(^1P_1) + NO \rightarrow Hg(^1S_0) + N + O$$

(27) $$N + N + (M) \rightarrow N_2 + (M)$$

(28) $$O + NO + (M) \rightarrow NO_2 + (M)$$

(29) $$NO + NO_2 \rightleftharpoons N_2O_3$$

The decomposition in an electric discharge is rather complex, and the experimental data appear in a number of cases to be in disagreement.[25–30]

THE EQUILIBRIUM CONSTANT

The equilibrium constant of the reaction:

(30) $$N_2 + O_2 = 2NO \quad (K = [NO]^2/[N_2][O_2])$$

has been calculated by Giauque and Clayton.[31] Numerous papers have appeared dealing with this equilibrium, primarily from the standpoint of calculation rather than actual measurement of the equilibrium.[32–38] The quantity of nitric oxide produced in a mixture of nitrogen and oxygen (assuming 80% nitrogen) has been calculated[39] from the data of Giauque and Clayton, with the results summarized in Table I.

Table I.—Production of Nitric Oxide from Oxygen and Nitrogen

T°K.	$K \times 10^4$	Volume % nitric oxide		
		20% O_2	10% O_2	5% O_2
1800	1·2	0·44	0·31	0·22
2000	4·1	0·81	0·57	0·40
2200	11·0	1·33	0·94	0·67
2400	25·1	2·00	1·42	1·00
2600	50·3	2·84	2·01	1·42
2700	68·7	3·32	2·34	1·66

The value of K at 298·1°K. is $5{\cdot}27 \times 10^{-31}$. Values of K have been determined in the electric arc in closed cycle experiments. The values of K varied with the current strength, although it was stated that no deviations from the mass action law occurred.[40]

By using data for the equilibrium constant K, and for the velocity of decomposition, it is of course possible to calculate the rate of formation of nitric oxide from a nitrogen–oxygen mixture. This is given by:

(31) $$dp_{NO}/dt = k(Kp_{N_2}p_{O_2} - p^2_{NO})$$

where k is the specific rate constant for the decomposition of nitric oxide, and the decomposition is assumed to be a bimolecular process. Table II shows the partial pressure of nitric oxide as a function of the furnace temperature and the time of residence in the furnace.[41]

Table II.—Rate of Attainment of the Equilibrium Concentration of Nitric Oxide in Air (80% nitrogen, 20% oxygen, by volume) at a Total Pressure of 1 *Atmosphere: p_{NO} in Atmospheres*

t sec.	2000°K.	2400°K.	2800°K.	3000°K.
100	$\sim 8{\cdot}5 \times 10^{-3}$	$\sim 2{\cdot}1 \times 10^{-2}$	$\sim 3{\cdot}9 \times 10^{-2}$	$\sim 5{\cdot}2 \times 10^{-2}$
10	$2{\cdot}9 \times 10^{-3}$	$\sim 2{\cdot}1 \times 10^{-2}$	$\sim 3{\cdot}9 \times 10^{-2}$	$\sim 5{\cdot}2 \times 10^{-2}$
1	$3{\cdot}0 \times 10^{-4}$	$2{\cdot}0 \times 10^{-2}$	$3{\cdot}8 \times 10^{-2}$	$\sim 5{\cdot}2 \times 10^{-2}$
10^{-1}	$2{\cdot}9 \times 10^{-5}$	$3{\cdot}9 \times 10^{-3}$	$3{\cdot}8 \times 10^{-2}$	$\sim 5{\cdot}2 \times 10^{-2}$
10^{-2}	$2{\cdot}9 \times 10^{-6}$	$3{\cdot}9 \times 10^{-4}$	$1{\cdot}2 \times 10^{-2}$	$3{\cdot}9 \times 10^{-2}$
10^{-3}	$2{\cdot}9 \times 10^{-7}$	$3{\cdot}9 \times 10^{-5}$	$1{\cdot}2 \times 10^{-3}$	$5{\cdot}0 \times 10^{-3}$
10^{-4}	$2{\cdot}9 \times 10^{-8}$	$3{\cdot}9 \times 10^{-6}$	$1{\cdot}2 \times 10^{-4}$	$5{\cdot}0 \times 10^{-4}$
10^{-5}	$2{\cdot}9 \times 10^{-9}$	$3{\cdot}9 \times 10^{-7}$	$1{\cdot}2 \times 10^{-5}$	$5{\cdot}0 \times 10^{-5}$
10^{-6}	$2{\cdot}9 \times 10^{-10}$	$3{\cdot}9 \times 10^{-8}$	$1{\cdot}2 \times 10^{-6}$	$5{\cdot}0 \times 10^{-6}$
Equilibrium partial pressure	$8{\cdot}5 \times 10^{-3}$	$2{\cdot}1 \times 10^{-2}$	$3{\cdot}9 \times 10^{-2}$	$5{\cdot}2 \times 10^{-2}$

The rate of cooling is clearly also of importance and must be great enough to minimize any shift in composition from that present in the reaction vessel. It may be assumed that formation of nitric oxide during the cooling process makes a negligible contribution to that already present. Since the nitric oxide represents only a small proportion of the total gases present, the oxygen content of the gases may be assumed to remain constant. The results of calculations on the decomposition of nitric oxide, as a function of cooling rate, are shown in Fig. 2 from which it is clear that for a reaction carried out at 2800°K. cooling rates of the order of 10^5 to 10^6 degrees per second are necessary to 'freeze in' 90% of the equilibrium content of the nitric oxide. In the presence of excess of oxygen (0·2 atm.) the cooling rates must be increased by a factor of about three.

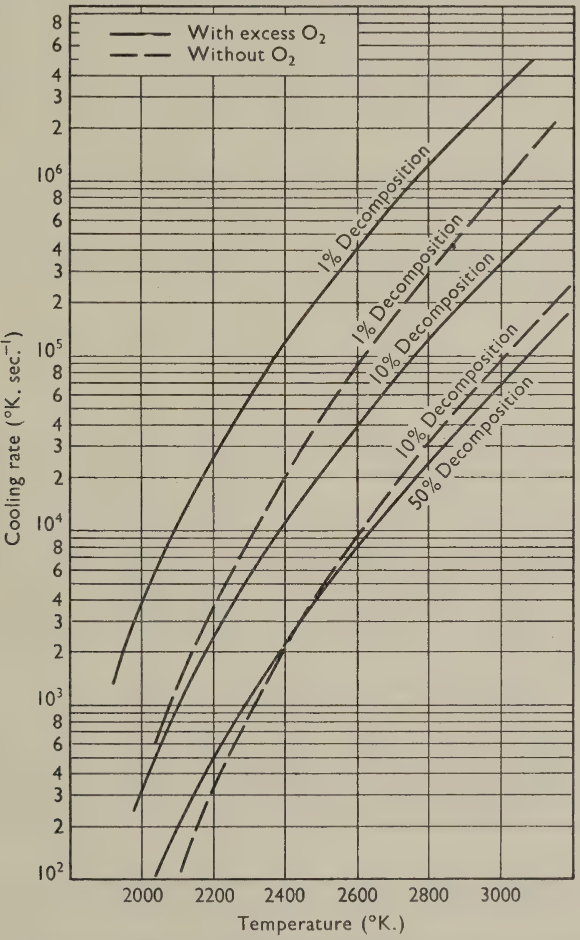

FIG. 2.—Decomposition of nitric oxide as a function of cooling rate (excess O_2 represents 0·20 atm.)

Clearly for high yields of nitric oxide high temperatures and high cooling rates are essential. For example, the equilibrium concentration of nitric oxide nearly doubles between 2400° and 2800°K., and at the latter temperature equilibrium is attained in about one-tenth of a second. At low cooling rates, however, the yield of nitric oxide is finally independent of the reaction temperature. High cooling rates might be conveniently attained by adiabatic expansion.

The Fixation of Nitrogen by Electrical Means

ARC DISCHARGE

The earlier work on electric arc furnaces, very fully treated in Mellor (VIII, 365), has been reviewed.[42, 43] It should be made clear at this stage that the mechanism of the arc process is still not known with any degree of certainty. The following discussion is therefore primarily chronological. It has been concluded[44] that 'electronic' modifications of nitrogen and oxygen, for example molecular or atomic ions or excited molecules, are necessary for reaction to occur, and the suggestion has been made that in the formation of nitric oxide in an electric discharge the thermal effect is relatively unimportant[45]; the existence of a chain mechanism has also been postulated giving as primary products dinitrogen pentoxide and ozone.[46] About the same time (1937) it was reported that the primary product in an electric discharge at 7 mm. Hg was only nitric oxide.[47] In the presence of excess of nitrogen, active nitrogen was reputed to be formed and removed part of the nitric oxide. Apparently the higher was the concentration of oxygen the more efficient was the removal of nitrogen. The mechanism of formation was thought to be by way of an activated oxygen molecule (formed by collision) and energy-rich nitrogen molecules formed from positive ions. In a spectroscopic examination of nitrogen–oxygen mixtures subjected to an electric discharge it was found that more NO and N_2^+ existed at higher frequencies[48] (up to 10^8 cycles per second). The nitric oxide was supposed to have resulted from the interaction of N_2^+ with an oxygen molecule. Methane–nitrogen–oxygen mixtures were also investigated.[49] Bodenstein[50] suggested a mechanism based on free atoms obtained in the arc:

(32) $$N + O_2 \rightarrow NO + O$$

(33) $$O + NO \rightarrow O_2 + N$$

(34) $$N + NO \rightarrow N_2 + O$$

In this reaction scheme the probability of splitting an oxygen molecule as compared with that for a nitrogen molecule was 1·77 to 1. In a more recent discussion (1947)[51] it was again proposed that the ion N_2^+ was responsible for the formation of nitric oxide in the arc. It is of interest that Partridge, Parlin and Zwolinski in 1954[52] said that little is known of the detailed mechanism of the reactions occurring in the electric arc, for example whether ions, molecular fragments or atomic fragments are the reactants. However, in a glow discharge in nitrogen contaminated with oxygen it appeared that two nitric oxide molecules could be formed, one in the ground state and the other in one of five activated states[53]:

(35) $$N_2 + O_2 \rightarrow \text{NO (ground)} + \text{NO (excited)}$$

The fixation process is affected by several variables, such as the frequency of the alternating current applied to the arc, whether the current is continuous or intermittent, the composition of the gas mixture and the nature of the electrodes. Observations on apparently similar systems are, however, frequently in direct opposition.

In general it has been found that high frequencies (up to 10^7 cycles per second) appear to favour higher yields of nitric oxide,[54, 55] possibly because the lower temperature diminishes the thermal destruction of nitric oxide. Similarly, general considerations in 1937[56, 57] favoured increasing the frequency of the current in the arc. This was again stressed in 1941,[58] partly on the basis of earlier work,[59] and certain analytical errors were pointed out. It was later reported[60] that on increasing the frequency in the range 50 to 10^6 cycles per second, the yield of nitric oxide increased from 28 to 40 g. per kw.-hr. In a study of the yield of nitric oxide as a function of frequency, a number of observations were made[61] and compared with those made on a direct current arc. At very low wattages the yield was said to be independent of the type of supply. At high wattages the alternating current arc apparently gave a lower yield, while in the intermediate range the frequency of the arc was related to the yield, showing a sharp maximum and minimum. The maximum was stated to be greater than the best yield obtained using a direct current arc. It has been reported that at very low frequencies a direct current discharge occurs in effect in each half-wave, and the nitric oxide yield is large.[62] The kinetic analysis of chemical processes in the electric discharge has recently been discussed.[63]

The rate of formation of nitrogen dioxide in a 2:1 oxygen–nitrogen mixture in the pressure range 4 mm. to 0·07 mm. Hg was found to be independent of the pressure, but proportional to the current.[64] Addition of oxygen in excess decreased the rate of reaction. Alternatively lowering the pressure of the gases has been said to improve the yield,[57, 58] and this effect has been attributed to the smaller amount of energy necessary to maintain a stable discharge at lower pressures.[65] Briner and Monnier[66] found that when mixtures of oxygen and nitrogen were circulated in an electric discharge the yield of oxides of nitrogen was nearly independent of the pressure and rate of flow of the gas. With rapid circulation of an equimolar oxygen–nitrogen mixture at 5–10 mm. Hg the yield of nitric oxide was found to be independent of the power.[67] Active nitrogen was stated to be produced during this reaction and it decomposed considerable quantities of nitric oxide.

The effect of electrode material used in the production of the arc is of much interest and has been quite extensively studied. As long ago as 1929[68] it was suggested that, since chemical reactions in electric discharges are electronic in nature, electrodes giving the greatest number of electrons at the lowest ionization potential would be the most efficient. This was experimentally verified. It has been found that lithium and barium oxide coatings on the electrodes are particularly useful for the efficient production of nitric oxide.[69] The addition of lithium, barium, calcium and silver in small amounts to copper electrodes apparently showed increases in the yield of up to 150%.[70] Spectrograms[71] indicated the importance of low ionization potential for the added metal. The use of electrodes of this type industrially has been discussed[57, 72, 73] and the fixation process has been studied as a function of frequency and electrode composition.[55, 65] Lithium salts are reputed to be particularly effective for coating the electrodes.[58] (The work function of a metal is of course closely related to its ionization potential.)

The general effect of temperature does not seem at all clear, probably owing to the difficulty of attaching a meaning to the term in an arc discharge. For example Henry[74] stated that the best yields of nitrogen dioxide were obtained at liquid air temperatures with a luminous discharge and an oxygen–nitrogen ratio of 2:1. However it has also been shown experimentally that in a high-frequency discharge the yield is independent of temperature.[75] However Briner and Monnier[66] show that the yield is decreased at low temperature. The reported fact that cooling with liquid air produces much ozone in a silent discharge while cooling with liquid oxygen produces much nitrogen dioxide[76] has been attributed to the rate-determining step being the oxidation of nitrogen to nitric oxide.[77] The discharge in liquid air has been studied[78, 79] and the following reactions have been suggested in which ozone and nitric oxide are primary products:

(36) $2NO + O_2 = 2NO_2$

(37) $3NO + O_3 = 3NO_2$

(38) $2NO_2 = N_2O_4$

(39) $2O_3 = 3O_2$ (explosively at $-100°$)

(40) $NO + NO_2 = N_2O_3$

(41) $2O_3 + 3N_2O_3 = 3N_2O_5$

In several cases 'catalysts' have been added to the arc discharge by spraying in a liquid or a finely divided solid.[80, 96] Examples of such 'catalysts' are copper and zinc, or copper and nickel.[81] The effect of modulating[82] or intermittently operating the arc[83] has been reported as leading to improved yields, for example by reducing unwanted side reactions.

The variation of gas composition has already been briefly mentioned. The yield has been stated to be affected by increase in the nitrogen or oxygen concentration.[75] Again the most rapidly reacting mixture was said to be one with 40% of oxygen.[64] Alternatively the yield of nitric oxide was found to show a sharp maximum at about 90% of oxygen.[84] In 1939 it was noted that the maximum yield is obtained from an 80% nitrogen–20% oxygen mixture.[85] In the presence of water the maximum was lower and practically flat from 40 to 90% of nitrogen. The position of the maximum from the point of view of composition was found to vary with wave-length of the discharge. For example at $\lambda = 236$ m. a maximum yield was obtained with a mixture consisting of 50% of oxygen and 50% of nitrogen, while at $\lambda = 293$ m. there were two maxima, with 37% and 20% of oxygen, respectively.[86]

Miscellaneous experiments have been carried out on the fixation of nitrogen via the oxides. For example the production of nitric oxide in the arc was found to be increased if the air was first ozonized,[87] or inhibited if 0·5% of fluorine was added to the air.[88] It has been shown that in a heated ozonizer nitric oxide may be produced at 745° to 1030°.[89] Nitric oxide was also produced when nitrogen and oxygen in admixture were exposed to the action of electrons.[90] Similarly the use of fast moving electrons has been proposed, in the presence of a catalyst.[91]

Chemical synthesis from free radicals produced in microwave fields has been studied,[92] as has the rate of production of nitric oxide in the Crookes dark space,[93] and the importance of nitric oxide for the carrier density of a low current arc in air has been mentioned,[94] as has the effect of rotating the electrodes during the discharge.[95] Nitric oxide was found to be one of the combustion products of the carbon arc in air.[96]

HIGH-FREQUENCY DISCHARGE

In 1938 an ultra high-frequency discharge was obtained[97] having the form of a narrow gas flame and described as a torch discharge. This type of discharge apparently operated at a lower temperature than the normal arc and was reputed to give higher yields of nitric oxide. The equilibrium point could be reached much more rapidly at higher pressures. It was again found that metals with low ionization potentials when used as electrodes gave higher yields, which were also said to be proportional to the size of the flame.[98] In a later paper by the same author,[99] the yields of nitric oxide as a function of time and energy were given. It was subsequently pointed out that the volume of the discharge was proportional to the power, and hence the increased nitric oxide found with increasing power was in fact due to increasing volume of the discharge.[100] This work appears to be in agreement with that of Serebryakov.[101]

A further apparently new type of discharge has been examined quite extensively by Cotton. Essentially four electrodes were situated symmetrically in a plane with one opposing pair connected to a high voltage (approximately 2000 v. 60 cycles per second) source while the other opposing pair was connected to a radio-frequency source (1–10 megacycles). The effect was to produce simultaneously crossed high and low frequency discharges. The phenomenon was referred to simply as a crossed discharge.[102] In the use of this type of discharge for the production of oxides of nitrogen it was found[103] that there appeared to be frequencies which were particularly advantageous for reaction, and independent of electrode material. There were also critical electrode frequencies[104] which appeared to be independent of the reaction type but dependent only on the electrodes. These have been fully discussed and correlated.[105–108] The operation of the discharge in the light of variables such as the concentration of nitric oxide obtained, the ratio of the high to the low frequency energy input, the shape of the electrodes, the type of electrodes and the pressure in the system has been examined.[109] More recently patents have been filed on the commercial importance of this type of discharge.[110–114] Subsequently (1954) the use of a very similar apparatus to that of Cotton gave very different results.[52] The authors could not obtain the discharge reported by Cotton and found that their discharge resembled a normal arc. The crossed discharge was found to enhance the nitric oxide yield over that obtained by high frequency alone, but no critical reaction or electrode frequencies were found and the yields were apparently 5 to 15 times smaller than those reported by Cotton. It was, however, found possible to operate the discharge at relatively high pressures.

Essentially industrial aspects of the fixation of nitrogen in an electric arc have been discussed.[115–130]

The Fixation of Nitrogen during Gaseous Reactions

In 1948 Gilbert and Daniels[39] published a paper on the fixation of atmospheric nitrogen in a gas-heated furnace. By the use of normal gaseous combustion it is possible to raise the temperature of air to about 1700°. If on the other hand the gases are preheated before combustion, temperatures in excess of 2100° may be obtained relatively easily. In this work two beds of magnesium oxide pebbles were used as the heat exchangers, whereby very rapid heating or cooling of the ingoing or outgoing gases respectively could be obtained. This research was apparently initiated at the suggestion of Cottrell who has developed the use of beds having a large ratio of surface area to volume.[131] The essence of the process is therefore to preheat the air in a pebble bed, to carry out the combustion so as to attain temperatures of at least 2100°, and then to cool very rapidly in a pebble bed to less than 1500°. Periodically the direction of flow in the beds is reversed. It is remarkable that under ideal conditions the issuing gases may be at temperatures as low as 100° to 300°, so that heat

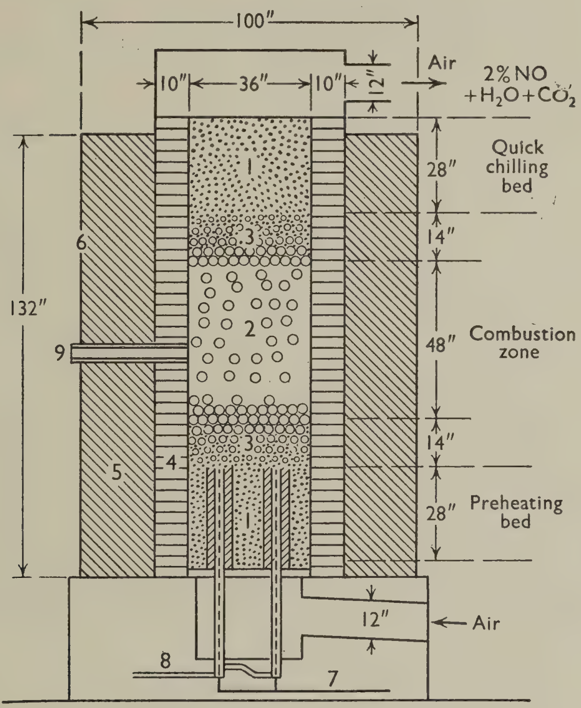

FIG. 3.—Furnace design showing upward air flow

1. 97% magnesium oxide ¼ in. pebbles
2. 97% magnesium oxide 2 in. spheres
3. 97% magnesium oxide ¼ in. to 2 in. spheres
4. 97% magnesium oxide bricks
5. Periclase insulation
6. Iron
7. Gas pipe inlet
8. Water cooling jacket
9. Water-cooled peep site

losses are not as serious as might at first be imagined. Rates of cooling in the pebble beds can be of the order of 20,000° per second. Various patents have been filed for beds operating on this principle.[132, 133] One of the difficulties in operation is to maintain the porosity of the bed, which may become quite rapidly choked with a crystal growth of magnesium oxide on the pebbles.[134] It has been suggested that the exit gases should be mixed with cool gas to minimize the decomposition of the nitric oxide.[135, 136, 137] Hendrickson and Daniels[138] have described the furnace shown diagrammatically in Fig. 3. The fuel gas is enriched water gas, having a total calorific value of about 500 B.T.U. per cubic foot. It is noteworthy that water cooling

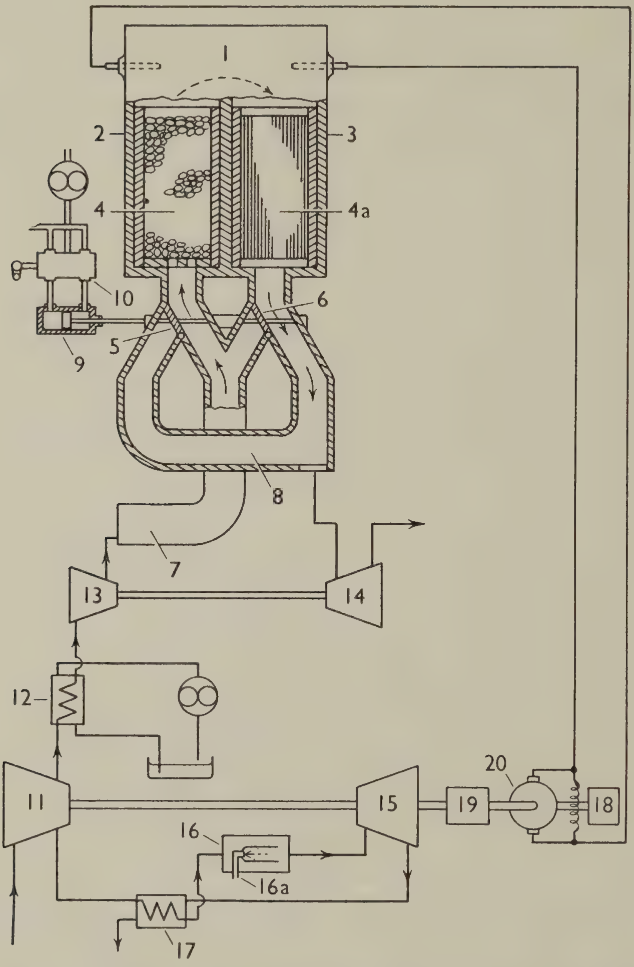

FIG. 4.—Apparatus for production of nitric oxide (arc process)

1.	Reaction chamber	11.	Main compressor
2, 3.	Regenerator chamber	12.	Inter-cooler
4.	Pebbles	13.	Auxiliary compressor
4a.	Refractory plates	14, 15.	Gas turbines
5, 6.	Valve gear	16.	Combustion system
7.	Air inlet duct	17.	Heat exchanger
8.	Outlet duct	18.	Starter
9.	Piston and cylinder	19.	Reduction gear
10.	Reversing valve	20.	Electric generator

of the gas inlet pipe is feasible even at the very high operating temperatures attained. The refractories are approximately 99% magnesium oxide. The flow of the gases is reversed every few minutes so that they are cooled, or heated, at the rate of about 20,000° per second. As it is impracticable to have fuel jets directed from above, owing to the buoyancy of the flame, fuel is injected only at every half cycle, when air is flowing upwards. The operating temperature is about 2200° and under these conditions it was found possible to operate the furnace for about a week. The product gases contain approximately 1·7% of nitric oxide. Again the main problem was the volatility of the magnesium oxide. More recently a flowing bed of pebbles has been used to reduce the choking of the gas flow channels.[139] The process has been developed to the stage of a demonstration plant capable of producing 40 tons of nitric acid per day, but the plant was later shut down as it was unable to compete with the improved Haber process.

A modified version of the method developed by Daniels recently patented (1955)[140] may be regarded as a combination of the arc process and pebble bed heat exchangers. This device is shown schematically in Fig. 4. The two beds flanking the reaction vessel may be used regeneratively, but the source of heat is used directly to heat the reacting gases in the reaction chamber rather than to heat the pebble beds. This design, it is claimed, avoids the necessity for the pebbles to withstand temperatures greater than 2000°. The reaction is carried out at a pressure of several atmospheres in an electric arc at about 3000°, the high pressures facilitating the reaction $2NO + O_2 \rightarrow 2NO_2$.

The use of gaseous explosions for the technical synthesis of nitric acid has been the subject of several papers and patents. The principles are clearly similar to those obtaining in the combustion flames. As long ago as 1922, explosions in a 300 litre bomb were used to produce nitric acid for the munitions industry.[141] Explosions of air with commercial gases,[142] and of oxygen and nitrogen with carbon monoxide,[143, 144, 148] or methane,[144–146, 149] or hydrogen,[147, 148] have been examined. The effects of pressure, of the dimensions of the vessel and of the presence of heat absorbers, moisture or hydrogen have been discussed.[149–151] Combustion with formation of nitric oxide has been discussed in several papers.[151–159] Miscellaneous examples include the production of oxides of nitrogen by the rays of the sun,[160, 161] in ultra-violet light,[162] during the oxidation of phosphorus,[163, 164] in the Bikini cloud,[165] during the thermal decomposition of ozone in the presence of nitrogen,[166, 167] and in an ultrasonic field.[168, 169] The last method of formation appears likely to repay further study. The formation of nitric oxide during adiabatic compression of nitrogen and oxygen has been inferred from conductivity measurements.[170]

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SECTION XXIV

NITROUS OXIDE

BY I. R. BEATTIE

NOMENCLATURE OF THE NITROGEN OXIDES

In the several sections of this chapter the physical and chemical properties of the oxides of nitrogen are considered individually. For this purpose the only oxides separately described are those which may be regarded as well-established chemical compounds, rather than reaction intermediates. This definition is taken, for example, to include the thermally unstable dinitrogen trioxide but to exclude nitrogen trioxide.

A brief indication of the nomenclature currently favoured in Britain has already been given (see p. 158). This is not fully in agreement with the recommendations of the International Union of Chemistry. The names which have been adopted by the I.U.C., and those occasionally used in American publications, are given in Table I, together with those employed in Mellor's original Treatise; continued use of the inaccurate names marked with an asterisk is not recommended.

Table I.—Nomenclature of the Oxides of Nitrogen

Formula	Name		
	Mellor	I.U.C.	American
N_2O	Nitrous oxide	Dinitrogen (mono)oxide	Nitrogen (I) oxide
NO	Nitric oxide	Nitrogen oxide	Nitrogen (II) oxide
N_2O_3	*Nitrogen trioxide	Dinitrogen trioxide	Nitrogen (III) oxide
NO_2	*Nitrogen peroxide	Nitrogen dioxide	Nitrogen (IV) oxide
N_2O_4		Dinitrogen tetroxide	Nitrogen (IV) oxide
N_2O_5	*Nitrogen pentoxide	Dinitrogen pentoxide	Nitrogen (V) oxide

There is a formal analogy with the oxyacids of nitrogen, and this has led to the so-called functional system of nomenclature, where for example dinitrogen trioxide would be called nitrous anhydride. This system is not be be encouraged, as it is only of limited use without becoming both clumsy and inaccurate. Table II shows the formal and true anhydrides of the oxy-acids of nitrogen.

Table II.—Formal and True Anhydrides of the Oxy-acids of Nitrogen

Acid		Formal anhydride	True anhydride
Hyponitrous	$H_2N_2O_2$	N_2O	—
Hydronitrous	H_2NO_2	NO	—
Nitrous	HNO_2	—	N_2O_3
Nitric	HNO_3	—	N_2O_5

Nitrogen dioxide is a true mixed anhydride of nitrous and nitric acids. The decomposition of hyponitrous acid leads to the formation of nitrous oxide but

N_2O and $H_2{}^{18}O$ do not undergo isotopic exchange. Further, the reaction between nitrous oxide and water to yield hyponitrous acid is thermodynamically unfavourable, a pressure of 10^{27} atmospheres leading ideally to a 0·001N. solution of the acid.[1] It is interesting to note that Lewis and Randall[2] say that starting with water and air, nitric acid should be formed, according to their thermodynamic calculations, until the concentration of the acid is about 0·1M.

It is possible to regard $(NO)_2$ as the formal anhydride of nitrohydroxylamic acid, $H_2N_2O_3$, although this is not particularly helpful. The production of sodium nitrosyl (NaNO), and the relationship between the nitrosyl ion (NO^-) and the hyponitrite ion ($N_2O_2{}^{2-}$) are not well understood. Although the ion NO^+ is frequently referred to as the nitrosonium ion, rather than the nitrosyl ion, it would be preferable to refer to the ion NO^- as the nitroside ion, to avoid ambiguity.

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1 Moeller, T., 'Inorganic Chemistry' (London), 1952, p. 614
2 Lewis, G. N. & Randall, M., 'Thermodynamics' (London), 1923, p. 568

THE PREPARATION OF NITROUS OXIDE

ATMOSPHERIC NITROUS OXIDE

It has been suggested that the presence of nitrous oxide in the atmosphere is due to the decomposition of compounds containing nitrogen.[1] A summary published in 1951 gives the evidence in favour of the view that the main source of nitrous oxide is escaping soil air.[2] The following cycle was proposed: (1) nitrous oxide which appears in the soil is a decomposition product of compounds of fixed nitrogen; (2) the gas escapes into the atmosphere; (3) under the action of ultra-violet radiation it is dissociated into nitrogen and oxygen; (4) it accumulates above the earth's surface until equilibrium is reached.[3]

More recently, the reactions:

$$O + N_2 + M = N_2O + M$$

and

$$O_3 + N_2 = N_2O + O_2$$

have been suggested as possible sources,[4] although the second reaction has been said to be too slow to account for the observed quantities of nitrous oxide.[5] However it is pointed out that bacterial reactions could account for the discrepancy, although Bates and Witherspoon suggest that the role of micro-organisms is negligible.[6] The most recent work (1954) attributes the atmospheric nitrous oxide to a reaction between nitrogen molecules and atomic oxygen produced by the photochemical decomposition of ozone.[7] The steady-state pressure of nitrous oxide in the atmosphere is approximately 5×10^{-7} atmospheres.

PREPARATION OF NITROUS OXIDE

Nitrous oxide is formed for example in the hypobromite[8, 9] or hypochlorite[9] oxidation of ammonium salts, during the decomposition of nitrocellulose[10–12] and in the decomposition of ethylenedinitramine.[13]

There are many methods of preparing nitrous oxide, and several of these are mentioned in the original Treatise (Mellor, VIII, 385). The reduction of nitrites or nitrates may lead to nitrous oxide, for example where stannous chloride or sodium amalgam is the reducing agent. A more suitable method is the decomposition of nitrites or nitrates of derivatives of ammonia, usually ammonium nitrate,[14, 15] which has been discussed under industrial aspects (see p. 158), as has also the occurrence of explosions in heating ammonium nitrate.[16] It has been reported that the catalytic decomposition of hydroxylamine results in the production of nitrous oxide and ammonia.[17] However the reaction of hydroxylamine with nitrites is more

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important. For example, nitrous oxide may be prepared by running sodium nitrite solution into warm hydroxylamine hydrochloride, passing the gas through potassium hydroxide solution and over solid potassium hydroxide, then through concentrated sulphuric acid, and finally over phosphorus pentoxide.[18] Alternatively, addition of oxygen may precede the passage through the hydroxide solution, with subsequent freezing followed by pumping off of the oxygen and fractionation.[19] The mechanism of the last reaction has been investigated.[20, 21]

The reaction between nitric acid and sulphamic acid has been reported to lead to the production of pure nitrous oxide in 100% yield, where the acid concentration is 73%.[22] Alternatively the reaction of potassium dinitrososulphite, $K_2(NO)_2SO_3$, with sulphuric acid may be used.[23] The only other method which need be mentioned here is the reaction between nitrite and azide.[24]

It is interesting that Tompkins in 1936 used the reaction between nitrite and hydroxylamine,[25] but in 1948 obtained his nitrous oxide from a cylinder.[26] Similarly Johnston and Weimer[27] in 1934 used the decomposition of potassium dinitrososulphite in acid solution, but Johnston and Grilly in 1946 made use of medical nitrous oxide.[28] It is in fact doubtful if in the future it will be found advantageous to prepare small amounts of nitrous oxide because it is readily available in a relatively high state of purity, by reason of its medical importance. Further, it is not difficult to purify. The majority of the recent papers on nitrous oxide deal with material obtained from cylinders. According to the purification procedure of Blue and Giauque,[29] the cylinder is connected to a vacuum fractionating column and the gas, after passing over phosphorus pentoxide, is condensed in a liquid air trap, the apparatus then being evacuated. The liquid is then distilled through the vacuum-jacketed fractionating column, the end fraction being rejected, and the material is sublimed into a fresh bulb, with rejection of the initial and end fractions, and finally cooled and evacuated at 10^{-5} mm. Hg. The product was estimated to contain less than 1 part of impurity in 100,000, on a mole basis.

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PHYSICAL PROPERTIES OF NITROUS OXIDE

Thermodynamic and Associated Data

Many authors have calculated the thermodynamic functions of nitrous oxide from spectroscopic data.[1–11] The most recent work is that of Pennington and Kobe,[9] which is substantially in agreement with earlier work, notably that of Blue and Giauque.[10] Values of the entropy and specific heat of nitrous oxide in the standard state of unit fugacity, as calculated by Pennington and Kobe,[9] are given in Table III.

Table III.—Values of the Molal Entropy and Heat Capacity of Nitrous Oxide

T°K.	S° g.-cal. deg.$^{-1}$	C_p° g.-cal. deg.$^{-1}$
273·16	51·760	8·952
298·16	52·556	9·232
500	57·775	10·965
1000	66·179	13·206
1500	71·734	14·142

where S° = entropy in the standard state, omitting nuclear contributions.
C_p° = heat capacity in the standard state at constant pressure.

Blue and Giauque[10] have determined the molal entropy of gaseous nitrous oxide and find that at the boiling point it has the value 47·36 g.-cal. deg.$^{-1}$. The value they calculated from spectroscopic data is 48·501, giving a difference of 1·14 g.-cal. deg.$^{-1}$, due to the fact that the solid is to some extent disordered. Complete randomness would lead to a value $\boldsymbol{R} \ln 2 = 1{\cdot}377$ g.-cal. deg.$^{-1}$, so that adjacent molecules have a certain amount of discrimination between the nitrogen and the oxygen. The values given here for the molal entropy are those to be used in calculations based on the Third Law, ignoring the nuclear spin contribution (for nitrogen the spin is unity) given by $\boldsymbol{R} \ln 9$.

In view of the disorder in the solid, it might be expected that the previous thermal history of the specimen would influence the heat capacity and heat of fusion. No such effect could be found experimentally.[12]

The heat of formation of nitrous oxide has been measured calorimetrically with the following results: $20{\cdot}5 \pm 0{\cdot}3$[13], $19{\cdot}74 \pm 0{\cdot}07$[14], $19{\cdot}52 \pm 0{\cdot}21$[15], $19{\cdot}52 \pm 0{\cdot}10$[16] kcal. mol.$^{-1}$, all at 20° and constant pressure. The values chosen in the National Bureau of Standards Circular 500[17] are shown in Table IV.

Table IV.—Selected Values for Thermodynamic Properties of Nitrous Oxide.
[These Data refer to 298·16°K. (25°)]

S° g.-cal. deg.$^{-1}$ mole^{-1}	C_p° g.-cal. deg.$^{-1}$ mole^{-1}	ΔH° kcal. mole^{-1}	ΔG° kcal. mole^{-1}	$\log_{10} K$
52·58	9·251	19·49	24·76	−18·149

The most recent work on the experimental determination of the specific heat of nitrous oxide is that of Blue and Giauque,[10] who compare their data with the results of several previous workers.[18–21] Specific heat data have been expressed by several empirical equations, without the addition of new experimental work.[22, 23] Table V contains values selected from the work of Blue and Giauque.[10]

Table V.—Heat Capacity of Crystalline Nitrous Oxide (from a Smooth Curve through the Experimental Points)

T°K.	C_p g.-cal. deg.$^{-1}$ mole^{-1}
20	1·51
100	9·90
180	13·98

The accuracy of several methods for the determination of specific heats has been discussed, and results are given over a wide range of temperatures.[24] The velocity-of-sound method[25] has recently been used, in the form of sustained oscillations, to give results of high accuracy. The initial work of Clark and Katz[26] was improved to yield a value for the ratio of the specific heats, C_p/C_v, given by:

$$\gamma = 1{\cdot}2744 + 2{\cdot}25 \times 10^{-3}p + 9{\cdot}73 \times 10^{-4}p^2$$

where p is the pressure of the gas in atmospheres.[27] This equation applies to a temperature of 25·3° and clearly yields a value of $\gamma_0 = 1{\cdot}2744$, to be compared with the spectroscopic value under the same conditions ($\gamma_0 = 1{\cdot}2733$). By including the mass effect of the gas it has been shown that even better agreement with the spectroscopic data may be obtained, $\gamma_0 = 1{\cdot}2736$.[28] Koehler found the value 1·2858 at 25° and 1 atm.[29]

Melting and Boiling Point, Vapour Pressure, Latent Heats, and Critical Constants

The data in Table VI are taken from the National Bureau of Standards Circular.[17]

Table VI.—Physical Properties Associated with Changes of State for Nitrous Oxide

Process	T° abs.	Initial state	Final state	p (mm. mercury)	ΔH kcal. mole^{-1}	ΔS g.-cal. deg.$^{-1}$ mole^{-1}
Fusion	182·30	cryst.	liq.	658·9	1·563	8·574
Vaporization	184·68	liq.	gas	760·0	3·956	21·42

Blue and Giauque[10] give a complete review of determinations of the boiling and melting points of nitrous oxide made prior to their work and quote a value for the melting point of 182·26° abs., with a vapour pressure of 65·895 cm. Hg. A more recent determination by Hoge[30] gives the triple point as 182·35° abs. at a pressure of 65·89 cm. Hg.

The vapour pressure of nitrous oxide has been determined by various investigators over several temperature ranges.[10, 30–33] Only the most recent work in each range is given here. The equation of Blue and Giauque[10] for the solid from 148·48° abs. up to the melting point is:

$$\log p\,(\text{atm.}) = -(1286/T) + 7{\cdot}24980 - 0{\cdot}0014038T$$

That of Hoge[30] from the triple point up to 236° abs. is:

$$\log p\,(\text{atm.}) = 4{\cdot}1375 - 656{\cdot}60/(T-26)$$

That of Cook[33] is:

$$\log p\,(\text{atm.}) = 4{\cdot}6258 - (858{\cdot}63/T)$$

applicable from 12° to the critical temperature (36·4°). In all cases T is in degrees absolute.

For the boiling point Blue and Giauque[10] give the temperature 184·59° abs., to be compared with the 184·695° abs. of Hoge.[30] The latent heat of vaporization and fusion respectively were 3·958[10] or 3·956[30] kcal. mole^{-1} at the boiling point and 1·563[10] kcal. mole^{-1} at the melting point (the figure in the abstract cited[10] is in error). Eucken and Donath give values for the latent heat of sublimation as 5·822 kcal. mole^{-1} at 135·5° abs., and 5·695 kcal. mole^{-1} at 160·0° abs.[34]

The orthobaric densities of nitrous oxide have been redetermined recently[33] and are reasonably in agreement with previous work.[35] Fig. 1 shows the relationship between the orthobaric density and the temperature. The literature relating to the critical constants of nitrous oxide has been reviewed,[36, 37] while Table VII gives the experimental results of Cook.[33] The carbon dioxide–nitrous oxide system has also been studied in the critical region.[38]

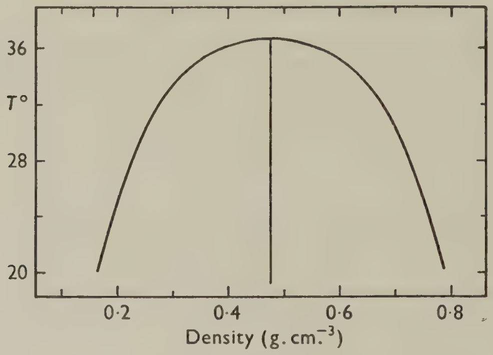

FIG. 1.—Orthobaric densities of nitrous oxide

Table VII.—Critical Constants of Nitrous Oxide

Temperature	Pressure (atm.)	Density (g. cm.$^{-3}$)	Volume (cm.^{3} mole^{-1})
36·4°	71·4	0·452	97·4

The surface tension of nitrous oxide, determined by capillary rise, has been given[39] over the range $-50°$ to $+20°$ by the approximate formula:

$$\gamma = 72{\cdot}8\,(1-T/311{\cdot}8)^{1{\cdot}26} \text{ dynes cm.}^{-1}$$

where T is in degrees absolute. At 30°, $\gamma = 0{\cdot}552$ dynes cm.$^{-1}$ and at $-50°$, $\gamma =$ 14·39 dynes cm.$^{-1}$ (The values given in the corresponding abstract[39] are erroneous and refer to variations in the constant, 72·8.)

Physical Constants Related to Properties of the Gas

The coefficient of volume expansion of an ideal gas is of course the reciprocal of 273·16. That of nitrous oxide has been found to be 3729×10^{-6} deg.$^{-1}$ at 76 cm Hg,[40] between 25° and 50°, referred to the volume of the gas at 0°.

The compressibility of gases has been extensively studied in view of the importance of the method of limiting densities in the determination of atomic weights. This method has recently been reviewed.[41] The compressibility of a gas is usually expressed in terms of λ or A, where these are given by the expression

$$\frac{p_0 v_0}{p_1 v_1} = \frac{1}{1-A} = 1+\lambda$$

where v_1 is the volume of 1 mole of gas at a pressure p_1 (equal to 1 atm.), and v_0 that in the limit as the pressure tends to zero. Nitrous oxide has been exhaustively studied in determinations of the atomic weight of nitrogen.[42–50] Recent values of the coefficient of compressibility, A, are $0{\cdot}0070_2$ at 0° (yielding an atomic weight for nitrogen of $14{\cdot}009_5$),[51] and 0·00576 at 22·05°.[52] These values may be compared with those of Cawood and Patterson[46] (1933), $0{\cdot}0070_9$ at 0° and $0{\cdot}0056_7$ at 21°.

As a generalization one may write

$$(pv) = (p_0v_0)(1-Ap)$$

where (pv) and $(pv)_0$ are values for the same mass of gas at pressures in the vicinity of 1 atmosphere and zero respectively. It is clear that there is a relationship between A and the second virial coefficient, B, in the expression

$$(pv)_m = RT+Bp$$

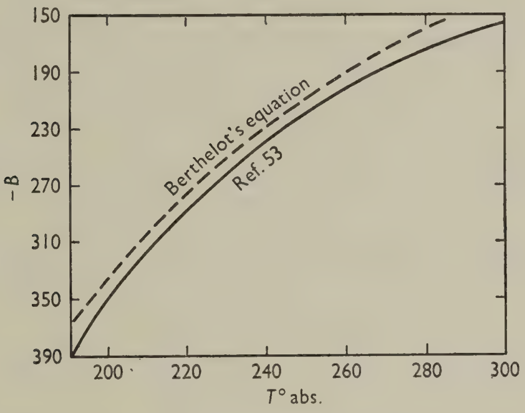

FIG. 2.—Second virial coefficients for nitrous oxide

The second virial coefficient of nitrous oxide is shown in Fig. 2 as a function of temperature.[53] (The corresponding equation given in the original paper is incorrect.) The experimental value agrees reasonably with Berthelot's equation of state, frequently used to correct for non-ideality. Volume changes on mixing gaseous carbon dioxide and nitrous oxide have also been studied.[54]

The viscosity of nitrous oxide has been measured by several investigators,[55–58] more recent results being those of Johnston and McCloskey,[59] and of Wobser and Müller.[60] Table VIII gives the smoothed values of the former investigators, who used the rotating disc method.

Table VIII.—Smoothed Values of the Viscosity of Nitrous Oxide obtained by the Rotating Disc Method[59]

T° abs.	Viscosity in g. cm.$^{-1}$ sec.$^{-1}\times 10^7$
180	898·2
200	998·7
220	1098·7
240	1197·7
260	1296·2
280	1393·3
300	1488·9

Their values at 290° abs. and 296·1° abs. respectively are $1441{\cdot}3\times 10^{-7}$ and $1470{\cdot}2\times 10^{-7}$ g. cm.$^{-1}$ sec.$^{-1}$, while Wobser and Müller[60] give 1462×10^{-7} g. cm.$^{-1}$ sec.$^{-1}$ at 293·2° abs.

The thermal conductivity of nitrous oxide is well established[61–64]; the values in Table IX are taken from the work of Johnston and Grilly.[65]

Table IX.—Smoothed Thermal Conductivity (k) Values for Nitrous Oxide (g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$)[64]

T° abs.	$k \times 10^5$
180	2·021
240	3·011
300	4·149
360	5·425
273·1	3·623
298·1	4·110

Recently the pressure dependence of the thermal conductivity has been determined, one result being that between 20 and 70 cm. Hg and at 1·8°C. the value is practically constant at $3{\cdot}62 \times 10^{-5}$ g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$.[66] With a larger variation in the pressure the results shown in Table X were obtained.[67]

Table X.—Variation of the Thermal Conductivity of Nitrous Oxide with Pressure (at 50°)[67]

p (atm.)	$k \times 10^5$ (g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$)
0	4·56
8·3	4·64
15·8	4·84
28·2	5·16
40·5	5·60
52·7	6·10

Self-diffusion coefficients of nitrous oxide do not appear to have been measured, although it is to be expected that data on the inter-diffusion of two such closely allied substances as nitrous oxide and carbon dioxide would not differ greatly from the self-diffusion of either pair. This is borne out by the experimental results shown in Table XI,[68] which are substantially in agreement with those of previous workers.[69, 70]

Table XI.—The Self-diffusion Coefficient of Carbon Dioxide and the Inter-diffusion of Nitrous Oxide and Carbon Dioxide

T° abs.	Carbon dioxide		Carbon dioxide–Nitrous oxide	
	D, cm.^{2} sec.$^{-1}$	p (mm.)	D, cm.^{2} sec.$^{-1}$	p (mm.)
194·8	0·0516	157·0	0·0531	203·7
273·2	0·0970	307·2	0·0996	319·7
312·8	0·1248	490·4	0·1280	510·0
			0·1280	323·3
362·6	0·1644	468·4	0·1683	507·4

It may be noted that the figures quoted for the nitrous oxide–carbon dioxide system are consistently about 2·6% higher than those for the self-diffusion of carbon dioxide. Andrussov[71, 72] has calculated the coefficient of self-diffusion of nitrous oxide at 0° and 760 mm. to be 0·0890 cm.^{2} sec.$^{-1}$. The inter-diffusion of bromine and nitrous oxide has been studied,[73] as has the separation by thermal diffusion of several gas mixtures containing nitrous oxide.[74–80]

Watson, Rao and Ramaswamy[81] give their results for the dielectric constant of nitrous oxide at 960 kc. per sec. and several different temperatures in the form $E=(D-1)\times 10^6$. These data are summarized in Table XII, where a molar polarization value is also given.

Table XII.—The Dielectric Coefficient for Nitrous Oxide as a Function of Temperature, at Zero Pressure

$E_0^{25°}$	$E_0^{-33°}$	$E_0^{-80°}$	$P^{25°}$ (c.c.)
1022	1039	1060	8·33

The dipole moment of nitrous oxide has recently been redetermined from the Stark splittings of rotational transitions in the microwave region,[82] yielding a value of 0·166 debye, which is more accurate than previous values (0·249,[83] 0,[84] 0·05,[85] 0·14,[86] 0·17[81]).

The refractive index in the microwave region has been measured, yielding a value for $(n-1)\times 10^6$ of 558, at 25,000 Mc./sec. and reduced to N.T.P.[87] By use of the approximate formula $n^2=D$ (exact where n and D are measured at the same wavelength), the corresponding value for the dielectric coefficient in the form $(D-1)\times 10^6$ is 1116. The index of refraction of nitrous oxide in the visible region has been given as 1·0005078 for $\lambda=5462{\cdot}3$Å. also at N.T.P.[88]

The magnetic susceptibility of the oxides of nitrogen has been measured by Soné,[89, 90] the result for nitrous oxide being $-0{\cdot}43\times 10^{-6}$ (diamagnetic) whether the state is liquid or gaseous.

The magnetic rotatory power of nitrous oxide has been re-examined[91] with results substantially in agreement with previous work.[92] The Verdet constant $\varLambda_0^{760}=7{\cdot}75\times 10^{-6}$ min, when $\lambda=5780$Å., while $\varLambda_M=5{\cdot}02\times 10^{-5}$ radian. On comparison with the results of previous work, the data for nitrous oxide are reputed to show that the rotation does not vary with change of state.

The depolarization ratio, $\varDelta$, is the ratio of the intensities of the horizontal and vertical components of scattered light. It is a measure of the anisotropy of a molecule. Two values for this ratio are 0·102[93] and 0·122.[94] These may be compared with those of previous workers.[95–100]

The Structure of Nitrous Oxide

Much of the early work on the physical properties of nitrous oxide was directed towards a solution of the question whether the molecule is symmetrical. It is now accepted to be unsymmetrical, NNO, and linear.[101–105] Early electron diffraction data, based on the model NON, gave N–N distances of 2·38Å.[106–108] The most recent work for $N \leftarrow r_1 \rightarrow N \leftarrow r_2 \rightarrow O$ yields $r_1+r_2=2{\cdot}32$Å. with r_1/r_2 lying between 0·925 and 1·08.[109] The distances predicted by Pauling[110] on the basis of the adjacent charge rule are $r_1=1{\cdot}12$Å. and $r_2=1{\cdot}19$Å., giving a ratio of 0·94. The N–N distance determined by microwave absorption spectra is 1·126Å. with an adjacent N–O distance of 1·191Å.[111]

The structure of solid nitrous oxide has been examined by *X*-ray techniques and a full crystal structure has been given.[112, 113] The scattering powers of nitrogen and oxygen are so close that they were not individually located. Initially the structure NON was erroneously assumed, owing to lack of other data, although this does not affect the value of the analysis. The crystal structures of nitrous oxide and carbon dioxide are closely similar and really differ only in that the nitrous oxide molecule in contrast with the carbon dioxide molecule has no centre of symmetry. The appropriate space groups are T^4-P2_13 for nitrous oxide and $T_h{}^6-Pa3$ for carbon dioxide. The formation of mixed crystals, or more accurately solid solutions, has also been examined.[114, 115] By using the crystallographic data the density of solid nitrous oxide may be calculated. The value obtained on the basis of a unit cell which is cubic and has an edge of 5·72A. is 1·56 g./c.c. at the temperature of liquid air. This can be compared with the value experimentally determined by Heuse[116] of 1·62 g./c.c. (20° abs.), and by Biltz, Fischer and Wünnenberg[117, 118] of 1·604 g./c.c. (78° abs.). *X*-Ray patterns of liquid nitrous oxide have also been examined.[119]

Miscellaneous Properties

The passage of electrons through gaseous nitrous oxide has been examined by several investigators, partly in connection with the fact that it exhibits a Ramsauer effect.[120–129] A study of the ionization of nitrous oxide by electron impact indicates an ionization potential of 12·9 ev. for $N_2O \rightarrow N_2O^+$.[130] The stopping power of nitrous oxide for alpha particles has also been examined[131–135] and will be mentioned later (see p. 207).

The dielectric constant of liquid nitrous oxide has been reported at 70° abs., with reference to a vacuum, as 2·023.[214] A study of the absorption spectrum of the liquid gave the following results[215]

λ	2275	2300	2325	2350 A.
Extinction Coefficient	0·37	0·23	0·14	0·09 (190·6° abs.)
Extinction Coefficient	0·29	0·20	0·13	0·09 (186·6° abs.)

Miscellaneous studies include the scattering of *X*-rays,[136] the stopping cross-section for protons,[137] the conditions for electric discharge,[138, 139] and the behaviour of ultrasonic waves.[140–150, 216] Vibrational relaxation times have been measured by a steady flow method.[151]

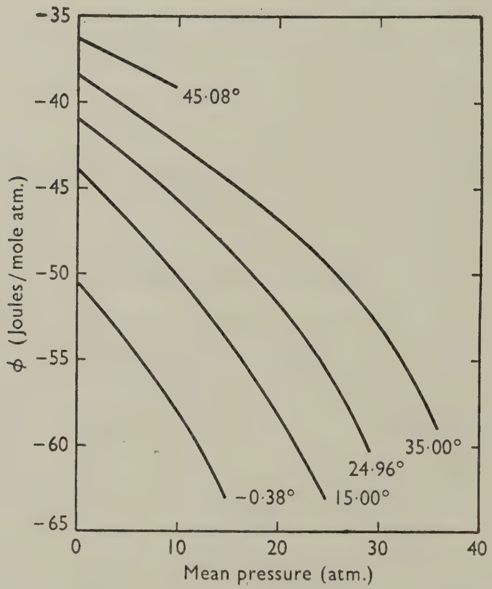

FIG. 3.—The dependence of the exothermal Joule–Thomson coefficient for nitrous oxide on pressure at various temperatures

The equilibrium constant for the reaction:

$$N_2{}^{16}O + H_2{}^{18}O \rightleftharpoons N_2{}^{18}O + H_2{}^{16}O$$

has been calculated.[152] The determination of the mass doublets ${}^{12}C_3H_8$–${}^{14}N_2{}^{16}O$ gave the value 0·06176+0·00009.[153] A recent determination of the Joule–Thomson coefficient for nitrous oxide yielded the results shown in Fig. 3.[154] The thermal conductivity of solid nitrous oxide has been measured between 90° abs. and 150° abs.[217]

Sorption Effects

Thermal accommodation coefficients for nitrous oxide have been determined on gold,[155] on bright platinum[156, 157] and on nickel oxide and quartz.[158] Adsorption on metal surfaces has been studied by several investigators; on nickel,[159–162] on platinum,[162, 163] on tungsten[163] and on iron.[164, 165] Sorption by carbon in various forms has been extensively examined,[166–173] as has the sorption by silica gel,[174, 175] aluminosilicates,[176] vitreous silica[177] and glass.[178–182] Various salts have been examined as sorbents for nitrous oxide, for example sodium chloride,[183, 184] calcium fluoride,[185] barium fluoride,[186] lead chloride,[187–188] and certain hydroxides and carbonates.[189] Because of its use as an anæsthetic, sorption in the presence of ether and chloroform has been studied.[190]

In connection with the solution of nitrous oxide in water, the crystal structure of the hydrate is of interest. Ordinary ice does not possess voids which are large enough to accommodate even the smaller molecules, such as methane.[191, 192] It appears that two distinct hydrate structures occur, dependent on whether larger molecules, such as $CHCl_3$ or C_2H_5Cl, or smaller molecules, such as Cl_2 or H_2S, are present. These have respectively, unit cell parameters of 17Å. and 12Å. (both being cubic).[193] For the structures based on a unit cell of 12Å., which is a modified body-centred cubic lattice, there are two sizes of void which may be filled, depending on the enclosed molecule.[194] The unit cell contains 46 molecules of water, having two small holes and 6 medium ones. Hypothetical hydrating numbers are given for all holes filled as $5\frac{3}{4}$, and for filling only the medium holes as $7\frac{2}{3}$. Nitrous oxide is interpreted as filling all holes, since the molecule is small. In view of the purely physical nature of this clathrate compound, it is interesting that there is no exchange between N_2O and $H_2{}^{18}O$ over a wide range of pH values.[195]

Solubility in water and aqueous solutions has been investigated quite extensively and many theories concerning so called hydration numbers have been advanced.[184, 196–198] The literature prior to 1927 has been reviewed.[199] However in view of the doubtful reliability of earlier work only more recent data are here given. Table XIII gives data on the solubility of nitrous oxide in water,[200] while Table XIV gives the corresponding data for aqueous salt solutions.[200] The Bunsen coefficient, a, is the volume of gas (reduced to N.T.P.) dissolved by unit volume of the solvent at the temperature of the experiment and under a pressure of 1 atm. The solubility may also be described in other ways; Markham and Kobe[200] define it as the volume of gas (reduced to N.T.P.) dissolved by the quantity of solution, of molality m, containing one gram of water (S_m).

Table XIII.—The Solubility (S_0) of Nitrous Oxide in Water

$T°$	S_0	a
0·2	1·2971	1·2970
25	0·5408	0·5392
40	0·3607	0·3579

These authors also found that they could represent their results satisfactorily by the relationship:

$$S_m/S_0 = cm + 1/(1+bm)$$

where c and b are constants for any given solute at the temperature of the experiment. These are the values shown in Table XIV.

Table XIV.—The Solubility of Nitrous Oxide in Aqueous Salt Solutions

	$T°$	c	b
NaCl	0·2	−0·0272	0·346
	25	−0·0167	0·280
	40	−0·0138	0·261
Na_2SO_4	25	−0·0746	0·834
	40	−0·0685	0·774
KCl	0·2	−0·0072	0·270
	25	+0·0001	0·211
	40	+0·0075	0·210
KNO_3	0·2	+0·0733	0·350
	25	+0·0243	0·170
	40	+0·0203	0·130
$Mg(NO_3)_2$	0·2	−0·0302	0·496
	25	−0·0252	0·310
	40	−0·0159	0·280
$MgSO_4$	0·2	−0·0844	0·800
	25	−0·0781	0·665
	40	−0·0848	0·586

The equilibrium pressure of the gas hydrate has been measured with the following result for $N_2O,6H_2O$[201]:

$$t° = 19{\cdot}4\,(\log p - 0{\cdot}9795)$$

where p is expressed in atmospheres. The rate of solution of nitrous oxide in water has also been examined,[202] the initial rate being given as 0·0120 c.c. min.$^{-1}$ cm.$^{-2}$ or 0·000141 g. h.$^{-1}$ cm.$^{-2}$ at 22°.

The solubility of nitrous oxide in non-aqueous solvents has been discussed[203] and measured. The results of Kunerth[204] are shown in Table XV where the solubility is given as volume in c.c. of gas dissolved, under existing barometric pressure and at the temperature specified, per c.c. of solvent under the same conditions.

Table XV.—The Solubility of Nitrous Oxide in Various Solvents

$T°$	Acetone	Acetic acid	Pyridine	Methyl alcohol	Ethyl alcohol	Benzaldehyde
18	6·30	5·00	—	3·38	3·07	3·23
24	5·50	4·55	3·45	3·23	2·85	3·00
30	4·46	4·11	3·17	2·98	2·61	2·78
36	3·23	3·75	2·94	—	2·33	2·59

$T°$	Aniline	Ethylene dibromide	Amyl acetate	*iso*Amyl alcohol	Chloroform
18	1·50	2·87	5·24	2·52	5·70
24	1·42	2·69	4·93	2·37	5·26
30	1·35	2·52	4·60	2·24	4·57
36	1·28	2·37	4·30	2·12	3·70

The solubility of nitrous oxide in *cyclo*hexanol has been reported as 735·84 c.c. per litre at 766 mm. of mercury.[205] Results for miscellaneous solvents have been given by Horiuti[206, 207] and are summarized in Table XVI.

Table XVI.—The Solubility of Nitrous Oxide in Certain Organic Solvents (c.c. Nitrous Oxide per c.c. of Solvent—Ostwald)

T°	Carbon tetrachloride	Chlorobenzene	Benzene	Acetone	Methyl acetate
10	5·26	3·891	4·453	7·64	8·035
25	4·285	3·174	3·686	5·95	6·27
40	3·565	2·650	3·123	4·73	4·95

The effect of nitrous oxide on the surface tension of water, ethyl alcohol, ether, carbon disulphide and carbon tetrachloride has been examined[208] by the capillary rise method. The solubility of nitrous oxide in nitrogen dioxide has been studied, in connection with the use of the resultant liquid as a low-temperature oxidant in rocket fuels.[209–211] Boron trifluoride and nitrous oxide do not react, but merely give a normal binary eutectic at $-138{\cdot}0°$ with a composition of 76·6% (mol.) of boron trifluoride.[212] Similarly the binary system N_2O–HCl was found not to show any evidence of compound formation.[213]

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THE DECOMPOSITION OF NITROUS OXIDE

It might be expected that the decomposition of a simple molecule such as nitrous oxide would require little discussion. There has however been much research on the decomposition, both in the presence, and in the absence, of catalysts. As recently as 1951 Johnston[1] believed that at low concentrations of nitrous oxide there is an important contribution from a heterogeneous first-order reaction, but the situation has been considered by Hinshelwood and Lindars,[2] who conclude that the reaction is homogeneous and that the thermal decomposition follows the relationship:

$$k = \frac{an}{1+a'n}+bn$$

where k is the formal rate constant for a first-order reaction and n is the initial concentration of nitrous oxide; a, a' and b are nearly constant.

Hinshelwood and Burk[3] originally supposed that the reaction was bimolecular, but complicated probably by the catalytic influence of certain by-products. The effect of the addition of powdered silica was, however, negligible. The rate-determining step was thought to be:

$$2N_2O = 2N_2+O_2$$

Lewis and Hinshelwood[4] later showed that the initial rate divided by the initial pressure is very nearly proportional to the reciprocal of the half-life. Since k has been written as a first-order rate constant, in the event of a second-order reaction k would be proportional to n, and k/n would be related to $1/t_{1/2}$. This argument assumes that the products do not affect the rate of reaction.

Above about 100 mm.[5] it is sufficiently accurate to write $k=A+bn$, where A is another constant. This expression holds up to a pressure of several atmospheres. However, the results of Nagasako and Volmer,[6] and in particular those of Hunter,[7] indicate that above about 5 atm. a considerable decrease in the variation of k with pressure occurs. The results of Hunter are in agreement with three separate quasi-unimolecular reactions and may be represented by the equation:

$$k = \frac{an}{1+a'n}+\frac{bn}{1+b'n}+\frac{cn}{1+c'n}$$

These reactions become independent of the pressure at 0·08, 5 and 30 atm. respectively. This tends to indicate that at least three separate modes of activation occur in this reaction. It is interesting to note here that Herzberg[8] has pointed out that since nitrous oxide is diamagnetic the reaction:

$$N_2O = N_2+O$$

involves the forbidden transition from a singlet state to a triplet state. This suggests that triplet states of nitrous oxide may be involved. The reaction: $N_2O=N+NO$ is similarly forbidden, but is further excluded[9] by the high dissociation energy of molecular nitrogen and the non-exchange of nitrogen atoms (by equilibration) during the decomposition of $^{15}N^{14}NO$.

Effect of Various Gases

The effect of various gases, including the inert gases, on the decomposition has been studied.[4, 13, 14, 15] Again the most recent experimental work is that of Hinshelwood and Lindars.[16] The experimental results are discussed very fully by the authors and it is sufficient here to state that the following equilibria and reactions are considered:

$$N_2O+N_2O \rightleftharpoons N_2O^*+N_2O$$

$$N_2O+X \rightleftharpoons N_2O^*+X$$

$$N_2O^*+N_2O \rightleftharpoons N_2O^{**}+N_2O$$

$$N_2O^*+X \rightleftharpoons N_2O^{**}+X$$

$$N_2O^* \rightleftharpoons N_2O^{3*}$$

$$N_2O^* + N_2O \rightleftharpoons N_2O^{3*} + N_2O$$
$$N_2O^* + X \rightleftharpoons N_2O^{3**} + X$$
$$N_2O^{**} \rightleftharpoons N_2O^{3**}$$
$$N_2O^{**} + N_2O \rightleftharpoons N_2O^{3**} + N_2O$$
$$N_2O^{**} + X \rightleftharpoons N_2O^{3**} + X$$
$$N_2O^{3*} \rightarrow N_2 + O$$
$$N_2O^{3**} \rightarrow N_2 + O$$
$$N_2O^{3*} + N_2O \rightarrow N_2 + O + N_2O$$
$$N_2O^{3*} + X \rightarrow N_2 + O + X$$
$$N_2O^{3**} + N_2O \rightarrow N_2 + O + N_2O$$
$$N_2O^{3**} + X \rightarrow N_2 + O + X$$

Molecules N_2O^* are regarded as sufficiently energized to be capable of transition to a triplet state, N_2O^{3*}. Correspondingly, molecules N_2O^{**} are to be regarded as capable of transition to a triplet II state, N_2O^{3**}.

The homogeneous decomposition of nitrous oxide is catalyzed by halogens,[17] and has been reported to be catalyzed also by mercury, but decreased by hydrogen.[18]

Heterogeneous Decomposition

The catalysis by powdered quartz has been studied,[10] and it has been suggested that in the presence of this substance less nitric oxide is formed than in the uncatalyzed decomposition.[11] Further, at low pressures (0·075–0·026 mm.) it was found that apparently the reaction in the *absence* of a catalyst is entirely heterogeneous.[12] Nevertheless it is experimentally easier to find a catalytic influence than not to find one, and the results of Musgrave and Hinshelwood[13] indicate that a 1600% increase in the surface area to volume ratio caused only a 10% increase in the rate. However the catalytic influence of nitric oxide was observed.[13]

The most recent results are those of Lindars and Hinshelwood,[2] who showed that a catalytic effect may be observed in certain reaction vessels made of a particular type of silica. They also note that the catalysis is easily recognized and may be eliminated.

The heterogeneous decomposition of nitrous oxide on platinum has been extensively studied.[10, 11, 19–29] The results generally are in accord with those of Hinshelwood and Prichard,[19] who found the reaction to be expressed by an equation of the form:

$$-\mathrm{d}[N_2O]/\mathrm{d}t = k[N_2O]/(1 + b[O_2])$$

It was further shown that the reaction is retarded, owing to the formation of a film of atomic oxygen. It has been suggested that the reaction is retarded more by oxygen produced in the reaction than by added oxygen,[24] and this has been attributed to the sorption of the former as oxygen atoms.[26] The reaction on gold was found to be a simple unimolecular reaction with no oxygen retardation,[30] while on silver, retardation occurs to the same extent whether the oxygen is added or results from the reaction.[31] The rate of decomposition on nickel has been reported to show a sharp rise at 359°, which may be related to the Curie point of nickel, 358–360°[32, 33]. The catalytic effect of copper has been studied and it has been suggested that only the fraction of the surface capable of sorbing oxygen with a high heat of sorption will effect the decomposition of nitrous oxide.[34] The catalysis on an iron–nickel alloy is unaffected by an external magnetic field.[35] As might be expected, the decomposition on oxide catalysts has been extensively examined, but the results are more difficult to interpret. Zinc oxide,[36–42] copper oxides,[36, 42–52] magnesium oxide,[36, 54, 56–58] nickel oxide[42, 46 52, 53] and other oxides[54–58] have been employed.

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Catalysis on bauxite has also been shown to occur,[59] but the reported catalysis by charcoal[60] is probably in error, since it has recently been shown that there is a first-order reaction between ashless carbon and nitrous oxide, yielding as the final products nitrogen and carbon dioxide.[61]

Photochemical Decomposition

The photochemical decomposition of nitrous oxide has been considered from the point of view of the reactions:

$$N_2O = N_2 + O$$

and

$$N_2O = NO + N$$

In the photosensitized decomposition in the presence of mercury vapour,[62] the overall reaction has been written:

$$Hg + N_2O = HgO + N_2$$

For the unsensitized decomposition, the following reactions have been suggested to explain the experimental results:

$$4N_2O = 2NO + O_2 + 3N_2$$ [63, 64]

$$4N_2O = 2{\cdot}8N_2 + 2{\cdot}5NO + 0{\cdot}7O_2$$ [65]

The absorption of light by nitrous oxide becomes appreciable below 2300 A., shifting to higher wave-lengths as the temperature is raised.[66] It seems probable that to explain the photochemical decomposition satisfactorily it is necessary to consider two primary processes.[67] The experimental work has been further discussed.[68, 69] It has been reported that infra-red radiation does not affect the rate of decomposition of nitrous oxide.[70]

The decomposition of nitrous oxide by alpha particles has been examined in the absence, and in the presence,[71, 72] of an electric field. It appears that the combination of oppositely charged ions plays no part in the decomposition. The effect of an electric discharge in decomposing nitrous oxide has been investigated,[73–81] as has the decomposition by cathode rays.[82]

It has been reported that at sufficiently high temperatures the decomposition of nitrous oxide becomes explosive.[83, 84]

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THE REACTIONS OF NITROUS OXIDE

The Reaction with Hydrogen

The reaction between nitrous oxide and hydrogen has been quite extensively studied, and although the details are not clear, the overall mechanism may probably now be correctly formulated. The main reaction is $H_2 + N_2O \rightarrow N_2 + H_2O$.

It is of interest that when hydrogen or ethylene is heated, under the same conditions and at pressures about 1 atm., the ignition temperature is almost the same whether nitrous oxide or oxygen is the oxidant.[1] It had already been pointed out that hydrogen and ethylene ignite in nitrous oxide at a temperature lower than the ignition temperature in air or oxygen. This is contrary to Davy's suggestion that all materials require a higher temperature for ignition in nitrous oxide, compared with that in air[2] or oxygen. It is also in sharp contrast with the results of Hinshelwood,[3] who found that in Jena glass bulbs the rate of interaction of nitrous oxide and oxygen at about 700° appeared to be determined by the thermal decomposition of nitrous oxide.

Melville[4, 5, 6] has studied this reaction and has concluded that in silica vessels a chain process is operative. He noted that the reaction is exothermic to the extent of 75 kcal. mole^{-1} and thus even more exothermic than the hydrogen: oxygen reaction (leading to the production of one mole of water) since only 45 kcal. is needed to dissociate one mole of nitrous oxide, whereas 60 kcal. is needed to produce one mole of oxygen atoms from molecular oxygen.

Melville's results exclude a simple reaction dependent on the dissociation of nitrous oxide, and the following reaction scheme is suggested:

Initiation
$$N_2O + N_2O \rightarrow N_2O^* + N_2O$$
$$N_2O + H_2 \rightarrow N_2O^* + H_2$$
$$N_2O^* \rightarrow N_2 + O$$
$$O + H_2 \rightarrow OH + H$$

Propagation
$$H + N_2O \rightarrow OH + N_2$$
$$OH + H_2 \rightarrow H_2O + H$$

Termination
$$H + H + M \rightarrow H_2 + M$$

The rate of the reaction at pressures between 50 and 400 mm. Hg was found to be proportional to the pressure of nitrous oxide, but nearly independent of the hydrogen pressure (at 550–700°). However, at lower pressures the rate is proportional to the square of the nitrous oxide concentration and unaffected by the addition of inert gases such as argon or nitrogen. It is retarded by packing the vessel in order to increase the surface area. The last effect indicates the termination of chains on the walls (see below).

EXPLOSION LIMITS

Melville did not find sharp explosion limits. The more recent work has however indicated the existence of such limits.[7,11] Using a powerful spark it was found that the limits are reproducible and only reasonably in agreement with earlier work,[8] where reproducibility may have been low owing to the use of too small a spark to cause ignition of mixtures near the limit. In Table XVII, which gives some of the data available, hydrogen and air mixtures are included for comparison.

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Table XVII.—Upper and Lower Explosion Limits of Mixtures containing Hydrogen and Nitrous Oxide near Atmospheric Pressure

Composition	Upper limit mole-% H_2	Lower limit mole-% H_2	Reference
H_2 + air	74·6%	4·19%	9
H_2 + (21% N_2O + 79% N_2)	29·0%	4·19%	9
H_2 + (42% N_2O + 58% N_2)	65·8%	4·38%	9
$H_2 + N_2O$	86·2%	5·8%	11
$H_2 + N_2O$	76%	5·2%	8
$H_2 + N_2O$	83·7%	—	7
$H_2 + N_2O$	79·7%	5·6%	10

It may be seen from this Table that the substitution of oxygen by an equal volume of nitrous oxide has no effect on the lower limit, while on the upper limit there is a considerable effect not solely due to the diminution of the total oxygen content of the mixture. The effect of additives on these reactions was also studied,[7, 9] and some of the results are summarized in Fig. 4. The explosion in the presence of nitric oxide or carbon monoxide has also been examined.[10] It has been shown that the spark ignition of nitrous oxide and hydrogen mixtures is mainly thermal, since non-branching occurs.[12]

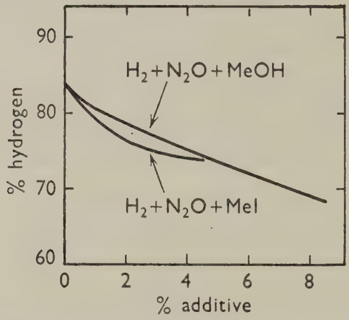

FIG. 4.—Effect of organic additives on H_2—N_2O explosion limits

The lower limit of explosions of nitrous oxide with hydrogen has been the subject of an extensive investigation by Fenimore and Kelso.[13] Their results are shown in Figs. 5 and 6 for two bulbs of different sizes. These workers found a minimum in the pressure–temperature curve for any given composition, and further observed that the explosive reaction was poisoned by oxygen, suggesting that the poisoning by oxygen from the thermal decomposition of nitrous oxide could account for this minimum. The presence of the HO_2 radical at a temperature some 200° higher than that at which it had previously been identified was therefore postulated. The reaction:

$$H + O_2 + M \rightarrow HO_2 + M$$

accounts for the poisoning, since the radical HO_2 is inert in not giving further radicals, and H is the only labile particle to react with molecular oxygen. That this poisoning is not due to paramagnetism is shown by the lack of influence of nitric oxide.

The reaction between hydrogen and oxygen is found to be sensitized by nitrous oxide. Nitrous oxide added to a hydrogen:oxygen mixture at 550° is reputed to behave as an inert gas. If however nitrous oxide and hydrogen are mixed, and oxygen is added, there is either an instantaneous ignition or alternatively an auto-

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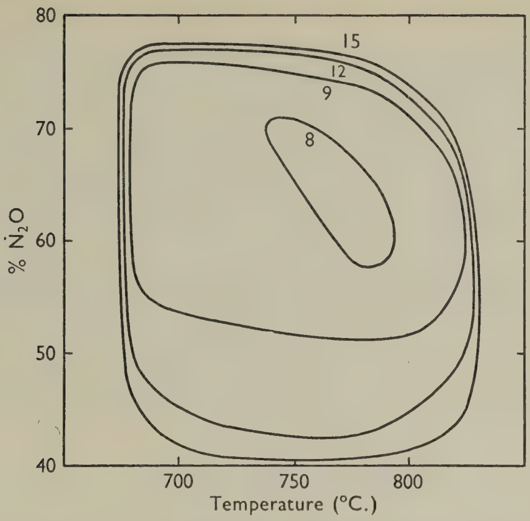

FIG. 5.—Lower explosion limit of N_2O—H_2 mixtures in silica vessels of 2·5 cm. internal diameter. Figures on the curves refer to pressures in cm. Hg.

catalytic reaction resulting eventually in an explosion.[14] The explosion occurs most readily when the hydrogen and nitrous oxide have been together for a long time and when the pressure of the added oxygen is low. It is suggested that the sensitizer is in fact nitric oxide,[62] formed by the reaction:

$$N_2O + H \rightarrow NO + NH$$

It is reported that in the presence of oxygen this reaction is inhibited.

The propagation of explosions of nitrous oxide and hydrogen through a system of glass and rubber tubes has been examined.[15]

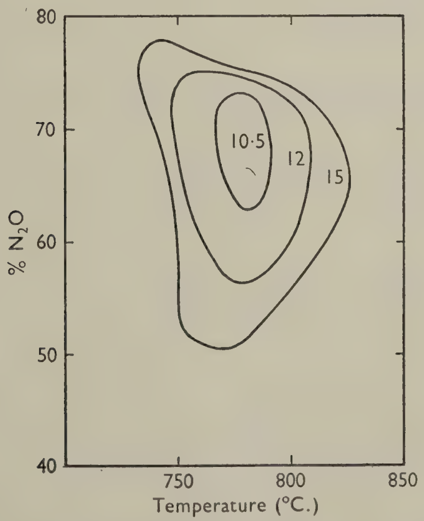

FIG. 6.—Lower explosion limits of N_2O—H_2 mixtures in silica vessels of 0·9 cm. internal diameter. Figures on the curves refer to pressures in cm. Hg.

THE PHOTOCHEMICAL REACTION

The photochemical reaction between nitrous oxide and hydrogen in the presence of mercury vapour has been investigated.[16, 17] Earlier work by Melville[5, 18, 19] indicated that the photochemical chain length agreed with that for the thermal reaction. At low pressures the reaction rate is proportional to the light intensity, while at higher pressures the rate is proportional to the square root of the light intensity, showing that the chains are ended by self neutralization. The dark reaction was found to be negligible. In a study of the different effects using hydrogen and deuterium,[19] no isotope effect that could not be interpreted in terms of a collision-frequency factor was observed.

In a more recent investigation[20] the mercury photosensitized decomposition has been studied in the range of 10–500 mm. Hg. The overall reaction is:

$$H_2 + N_2O \rightarrow H_2O + N_2$$

The following reaction scheme is proposed:

$$\begin{aligned}
&Hg + h\nu \rightarrow Hg^* \\
&Hg^* + H_2 \rightarrow Hg + 2H \\
&Hg^* + N_2O \rightarrow Hg + N_2 + O \\
&O + H_2 \rightarrow OH + H \\
&H + N_2O \rightarrow N_2 + OH \\
&OH + H_2 \rightarrow H_2O + H \\
&2H + M \rightarrow H_2 + M
\end{aligned}$$

It has been suggested that the reaction:

$$H + N_2O \rightarrow N_2 + OH$$

must have a considerable activation energy even though it obeys the spin rule and is exothermic.[21]

In the photochemical reaction between nitrous oxide and hydrogen, in the absence of mercury, both water and ammonia may be formed, although in the presence of sufficient hydrogen the reaction may be written:

$$N_2O + H_2 \rightarrow N_2 + H_2O$$ [22]

Again, in the presence of sufficient hydrogen, no nitric oxide bands are observed. The probable reaction mechanism is thought to be:

$$\begin{aligned}
&N_2O + h\nu \rightarrow N_2 + O \\
&\qquad\qquad (\rightarrow NO + N) \\
&O + H_2 \rightarrow H_2O \\
&N + H_2 \rightarrow NH_2 \\
&NH_2 + H_2 \rightarrow NH_3 + H \\
&NH_2 + NO \rightarrow N_2 + H_2O \\
&O + O + M \rightarrow O_2 + M \\
&N + N + M \rightarrow N_2 + M \\
&N + N_2O \rightarrow NO + N_2 \\
&N + NO \rightarrow O + N_2
\end{aligned}$$

The interaction of nitrous oxide and hydrogen under the influence of an electric discharge has also been investigated.[23]

THE CATALYSED REACTION

As is to be expected, the catalytic hydrogenation of nitrous oxide has been quite fully examined. The earlier work[3, 24, 25] has been reviewed.[26] Melville[27] has studied the reaction of deuterium and of hydrogen with nitrous oxide on a nickel wire catalyst. The velocity of the reaction with hydrogen is found to be about twice that with deuterium, which is explicable on the basis of zero-point energies. This result may be compared with the equal rates found for the photochemical reaction where atoms are involved. The most recent work is that of Dixon and Vance,[28] who noted that at one extreme the reaction may be approximately independent of the hydrogen pressure, owing to the amount of hydrogen adsorbed on the surface of the catalyst, while at the other extreme the primary process may be the decomposition of nitrous oxide on the catalyst, so that the rate is nearly independent of the nitrous oxide concentration, as found by Benton and Thacker.[26] Between these two extremes the mechanism changes, depending upon which gas is in excess.[3, 25, 29]

The reaction of nitrous oxide with hydrogen on alumina has also been studied.[30]

Miscellaneous Reactions

The reaction of nitrous oxide with carbon disulphide shows the existence of upper and lower explosion limits, the intensity of the light emitted being proportional to the square of the pressure.[31] This mixture has been examined as a possible rocket fuel.[32, 33]

With carbon monoxide the reaction is again said to be explosive,[34] and explosion limits have been studied.[35] It appears that in silica vessels at about 550° there is a surface reaction in which carbon monoxide is strongly sorbed. More recently Fenimore and Kelso[36] have examined the chemiluminescence of the reaction in vessels coated with sodium chloride or bromide, when sodium resonance lines are emitted. Catalysis by copper has also been studied.[37]

Sorption of nitrous oxide by carbon has already been mentioned (see p. 199), and this is closely related to the reaction of nitrous oxide with carbon. Charcoal may be burned in nitrous oxide.[38] The reaction of nitrous oxide with carbon[39] has been examined by Strickland-Constable.[40–42] General work in this field has been reviewed.[43] The reactions of nitrous oxide with charcoal are in fact very similar to those occurring with oxygen.

The reaction of ammonia with nitrous oxide is important as a possible hazard in the manufacture of sodium azide.[44] Flame propagation[45] and abnormally high electronic excitation[46] have been studied.

The general reactions of nitrous oxide as an oxidizing agent in the gaseous phase have been investigated.[47]

The oxidation of arsenic by nitrous oxide is said to become appreciable at 250–270°, with ignition occurring at 400–450°.[48] No chemi-luminescence is observed, and there is no upper critical oxidation pressure as is found with oxygen. It appears that the reaction occurs on the surface and is not dependent on the primary decomposition of the nitrous oxide.

The effect of nitrous oxide on the lower critical oxidation limit of phosphorus vapour has been examined,[49] and the interaction of phosphorus and nitrous oxide in a silent electric discharge has been shown to commence at a certain characteristic potential.[50]

According to Nichols and Derbigny[51] (1926) nitrous oxide may be reduced by aqueous solutions of titanous chloride, stannous chloride or sodium sulphite, to yield respectively ammonia, hydroxylamine or nitrogen, with no side reactions. The rate of reaction is increased by raising the temperature or increasing the concentration of the reagents. In the case of stannous chloride and titanous chloride the rate decreases with increase in the concentration of acid. Saturated hydrogen sulphide solutions have been said to reduce nitrous oxide completely to nitrogen and ammonia.[52]

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Rates of reaction of excited mercury with nitrous oxide have been observed,[53] and the reaction of this gas with sodium atoms, which is chemi-luminescent,[63] has been said to follow the reaction scheme[54]:

$$\begin{aligned} &Na + N_2O \rightarrow NaO + N_2 \\ &NaO + Na_2 \rightarrow Na_2O^* + Na \\ &Na_2O^* + Na \rightarrow Na_2O + Na^* \\ &Na^* \rightarrow Na + h\nu \end{aligned}$$

One of the most interesting reactions of nitrous oxide is that with sodamide to yield sodium azide. Reaction also occurs between metallic potassium solutions in liquid ammonia and nitrous oxide, again to yield an azide.[55] Although the reaction is complex, the probable first step is the formation of potassium amide, which is soluble in liquid ammonia:

$$2K + N_2O + NH_3 \rightarrow KNH_2 + KOH + N_2$$

The amide then reacts with nitrous oxide to give the azide and more of the insoluble hydroxide:

$$2KNH_2 + N_2O \rightarrow KN_3 + KOH + NH_3$$

This type of reaction is now of commercial importance for producing sodium azide.

The reaction of nitrous oxide with nickel has been stated to involve the formation of a difficultly permeable film.[56] With atomic chlorine the reactions suggested are[57]:

$$\begin{aligned} &Cl + N_2O \rightarrow ClO + N_2 \\ &ClO + ClO \rightarrow Cl_2 + O_2 \end{aligned}$$

The rate of decomposition of calcium carbonate is said to be catalytically affected by the presence of nitrous oxide.[58, 59] The reactions of nitrous oxide as the oxidant, with reductants such as lithium hydride, aluminium borohydride, monosilane, diborane, hydrazine, dimethylberyllium and various elements, have been examined for their possible value in rocket propulsion.[60] The reaction between titanium carbide and nitrous oxide is of first order.[61]

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SECTION XXV

NITRIC OXIDE

BY I. R. BEATTIE

FORMATION AND PREPARATION

Nitric oxide is formed during the decomposition of many organic substances containing both oxygen and nitrogen.[1–7] Its production in the combustion of various gases in air, and by the passage of an electric discharge through a mixture of nitrogen and oxygen, has already been discussed. Miscellaneous methods of formation include the decomposition of nitrosyl chloride,[8, 9] the incomplete combustion of substances in nitrogen dioxide[10] and the reduction of nitrites or nitrates, as for example in the reactions of metals with nitric acid.[11]

A survey of the recent literature reveals that there is no single preferred method for the preparation of nitric oxide. The methods generally used have been derived, in the majority of cases, from the improvement of historically well-known reactions. One notable exception is a suggestion by Ogg and Ray[12] who obtain nitric oxide by heating a dry powder in a Pyrex tube, which may be conveniently connected directly to a vacuum system. The reaction used is:

$$3KNO_2 + KNO_3 + Cr_2O_3 \rightarrow 2K_2CrO_4 + 4NO$$

It is found necessary in practice to add to the mixture ferric oxide previously calcined at 950°, and the chromic oxide is similarly calcined. The mixture suggested as an optimum composition is 63·75 g. (0·750 mol.) of potassium nitrite, 25·5 g. (0·250 mol.) of potassium nitrate, 76 g. (0·50 mol.) of chromic oxide and 120 g. (0·752 mol.) of ferric oxide. This mixture, with the addition of water, can be moulded into sticks or pellets which maintain their shape on drying and subsequent evolution of nitric oxide. It is, however, necessary to dry the mixture at 100° if anhydrous nitric oxide is required. As an example of this method, 10 g. of the mixture, heated with a luminous gas flame, yielded 872 c.c. of gas at 25° and 1 atm. pressure. The purity was estimated to be 99·8%.

A simple glass apparatus for preparing small quantities of various gases, including nitric oxide, has been described.[13] The reaction of boron nitride with various oxides, yielding nitric oxide, is of little but historical interest.[14, 15] However, the direct reaction between concentrated sulphuric acid and sodium nitrite has been used in the preparation of pure nitric oxide.[16, 17] As is to be expected in this method, considerable quantities of nitrogen dioxide are produced. The amount of nitrous oxide is very small, however, and nitrogen dioxide is readily removed. The procedure adopted for the removal of nitrogen dioxide[17] was washing with water followed by a double wash with concentrated sodium hydroxide solution. The gas was subsequently treated with concentrated sulphuric acid, passed over refrigerated silica gel and finally condensed with liquid air.

Preparation from Acidified Nitrite and Ferrous Salt

More usual methods of preparation involve the reaction of nitrite with acid in the presence of either ferrous ion or an iodide. The reaction:

$$Fe^{++} + HNO_2 + H^+ \rightarrow Fe^{+++} + NO + H_2O$$

has been examined[18] and its use in the preparation of nitric oxide fully discussed.[19] The apparatus suggested is shown in Fig. 1; for the quantities suggested, the volume of the generator and the reservoir may be about 750 ml. In operation the taps are opened and 6N-sodium hydroxide solution is added through the levelling bulb until the nitric oxide reservoir is nearly filled. The burette is then filled with water to the zero level, and the screw clip is closed. About 20 ml. of water is added to the generator flask. The two filling cups are charged with 10 ml. of each of the following solutions:

(1) 278 g. of $FeSO_4,7H_2O$ and 55 ml. of concentrated sulphuric acid made up to a total volume of one litre with water.

(2) 69 g. of sodium nitrite in one litre of water.

At this stage the levelling bulb is lowered and the two reagents are allowed to mix in the flask, when the levelling bulb is raised. To conserve the sodium hydroxide in the drying train, the first portions of the impure nitric oxide are expelled to the atmosphere through one of the filling cups. After expelling the first 200 ml. of gas, the apparatus is ready for use by the addition of fresh reagents. The generator should not be allowed to become more than one-third full of spent reagents before drawing them off, leaving only about 20 ml. as the residue. The gas may be dried by means of phosphorus pentoxide.

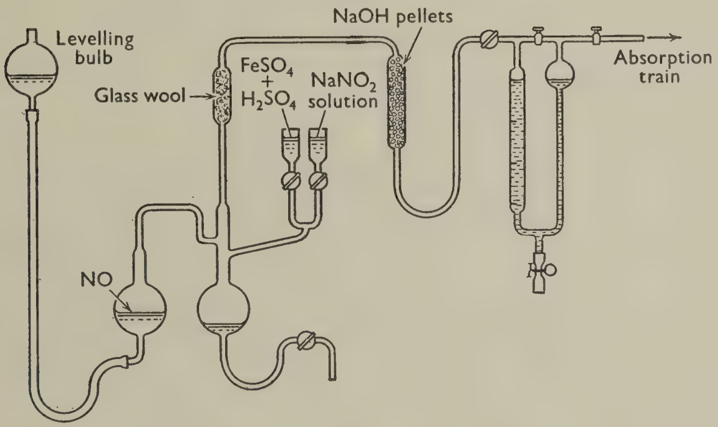

FIG. 1.—Apparatus for the preparation of nitric oxide

The burette is part of a metering device for measuring the quantity of gas which has been passed. The middle tap of the device is closed, so that nitric oxide bubbles through the meter, sweeping out any air. The tap on the far right is now closed, the centre one opened and the water level returned to the zero mark. By suitably opening either tap on the right or the centre tap, the quantity of nitric oxide passing to the absorption train may be measured.

Preparation from Acidified Nitrite and an Iodide

An important method for the preparation of nitric oxide, developed by Johnston and Giauque[20] and others, depends on the reaction:

$$2NO_2^- + 4H^+ + 2I^- \rightarrow 2NO + I_2 + 2H_2O$$

It has been shown that this reaction takes several hours to go to completion.[21] The action of nitrogen dioxide on solid potassium iodide and on a solution of potassium iodide has been studied[22] and may be represented by:

$$2N_2O_4+2KI \rightarrow 2KNO_3+2NO+I_2$$

and

$$N_2O_4+2KI \rightarrow 2KNO_2+I_2$$

In the solid state up to 4% of nitrogen may be formed, while in solution only about 1% is produced.

According to Johnston and Giauque,[20] a 20 l. glass container, evacuated and suitably shielded, is half-filled with a solution of 5 kg. of potassium nitrite and 2·5 kg. of potassium iodide in 15 l. of boiled out distilled water. A 50% solution of sulphuric acid is then run slowly into the solution from a reservoir, when nitric oxide is produced while iodine is precipitated and crystals of potassium sulphate are also formed.

The purification stages are primarily designed to remove nitrogen, other oxides of nitrogen and moisture. The gas is first bubbled through a long column of 90% sulphuric acid, through a similar column of 50% potassium hydroxide solution, and then passed through a trap held at solid carbon dioxide temperature to retain much of the moisture, and also the higher oxides which might have passed through to this stage. The gas is then condensed in a suitable bulb until sufficient has collected for the next stage, which consists in distilling the vapour through a glass tube about two metres long packed with phosphorus pentoxide and glass wool, the first and last fractions being rejected. The nitric oxide is then distilled into a bubbling tube to a depth of about 5 cm., and the remainder is slowly bubbled through the liquid. Two stages of bubbling are included in each complete cycle. The nitric oxide is then condensed, pumped on and sublimed before return to the beginning of the cycle. In general, three such cycles are regarded as producing nitric oxide of sufficient purity. For the experimental work the middle fraction only was used, and by physical means it was found that a final purity of at least 99·999% was attained. Fig. 2 illustrates a rather less rigorous procedure for the same preparation.

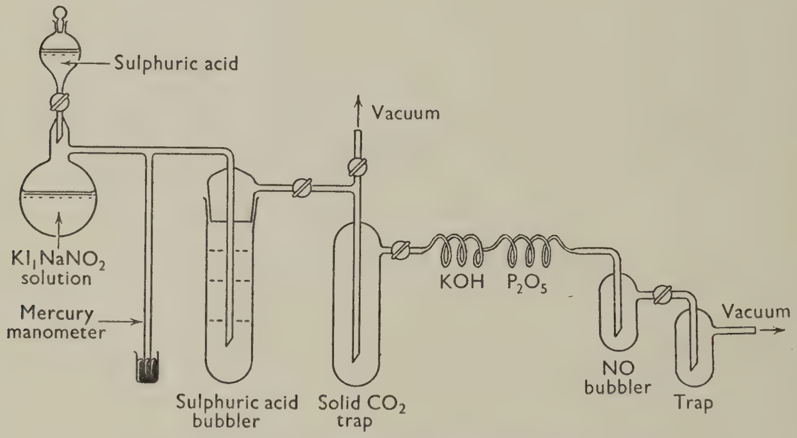

FIG. 2.—Apparatus for the preparation of nitric oxide

The reaction:

$$2Ba(NO_2)_2+I_2\ (\text{liq.}) \rightarrow Ba(NO_3)_2+BaI_2+2NO$$

taking place at 225°, has been studied.[23] Another allied reaction may be written:

$$2NOX+2I^- \rightarrow 2NO+I_2+2X^-$$

where NOX represents a nitrosyl compound such as the halide, acetate, fluoborate or thiocyanate.[24]

It has been suggested that pure nitric oxide may be obtained by the hydrolysis of nitrites, notably those of ferrous iron and beryllium (at 20°), of aluminium and cupric copper (at 60°), and of tin and magnesium (at 100°).[25] For example, by adding a saturated solution of sodium nitrite at a uniform rate to a saturated solution of ferrous sulphate containing excess of the solid salt and 1 part of sulphuric acid per 2000 parts of solution, nitric oxide is evolved and has a purity of 95% after 20 minutes and of about 100% after an hour. It has been suggested that a suitable reaction mixture for preparing nitric oxide on the lecture table consists of 52 g. of ferrous sulphate heptahydrate and 25 g. of sodium nitrite.[26]

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PHYSICAL PROPERTIES

Thermodynamic Functions

The heat capacity of nitric oxide has been measured by relatively few workers,[1–6] although numerous calculations from spectroscopic data have been made.[7–18] There are several good reviews of the literature,[19–25] but it should be noted that the results given by Spencer[22] appear to differ from the generally accepted values given by Witmer.[28] The spectroscopic data for nitric oxide are well known,[26] but two subsequent calculations[9, 10] have been shown to be incorrect owing to an erroneous interpretation of a doublet separation.[27] The data given in Table I are those of Witmer[28] and apply to the gas in the ideal state at unit fugacity.

The value obtained for the entropy at 298·1° abs. by Johnston and Chapman[9] is 50·35 g.-cal. mol.$^{-1}$ deg.$^{-1}$, in which Witmer found an error of less than 0·01 g.-cal mol.$^{-1}$ deg.$^{-1}$ This result may be compared with the value 50·43 g.-cal. mol.$^{-1}$ deg.$^{-1}$ of Johnston and Giauque.[4] It is of interest that the entropy measured calorimetrically by these investigators was 42·94 g.-cal. mol.$^{-1}$ deg.$^{-1}$ at the boiling point, which when corrected for non-ideality of the gas became 43·03. The corresponding figure calculated from spectroscopic data is 43·75 g.-cal. mol.$^{-1}$ deg.$^{-1}$, showing a

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Table I.—Heat Capacity and Entropy of Nitric Oxide

T° abs.	C_p g.-cal. mol.$^{-1}$ deg.$^{-1}$	S g.-cal. mol.$^{-1}$ deg.$^{-1}$
50	7·618	36·91
100	7·711	42·28
150	7·442	45·36
200	7·272	47·47
300	7·133	50·39

discrepancy of 0·72 entropy units. This will be discussed further under the structure of nitric oxide in the solid state. Some of the results of Giauque and Johnston for the solid and the liquid are shown in Table II.

Table II.—Heat Capacity of Solid and Liquid Nitric Oxide

T° abs.	C_p g.-cal. mol.$^{-1}$ deg.$^{-1}$
52·64	5·543
73·24	6·760
108·39	9·456
120·56	18·667

The figures chosen by the National Bureau of Standards are given in Table III.[29]

Table III.—Selected Values for the Thermodynamic Functions of Nitric Oxide, at 298·16° *abs.*

kcal. mol.$^{-1}$		$\log_{10} K$	g.-cal. mol.$^{-1}$ deg.$^{-1}$	
ΔH°	ΔG°		S°	C_p°
21·600	20·719	−15·18688	50·339	7·137

The heat of dissociation of nitric oxide as determined[190] by burning samples of red phosphorus in nitric oxide is 21·8 kcal./mole at 25°.

The velocity of sound in nitric oxide[35] has been studied with results exemplified in Table IV.[36]

Table IV.—The Velocity of Sound in Nitric Oxide, m. sec.$^{-1}$

Pressure (mm.)	t° 16·0	t° 1·0
754	332·40	—
649	—	323·49
398	—	323·60
219	332·72	—

The heat capacities in g.-cal. mol.$^{-1}$ deg.$^{-1}$, obtained by extrapolation to zero pressure, are 7·175 at 16·0° and 7·216 at 1·0°. These results may be compared with a value of 333·9 m. sec.$^{-1}$ at 16·3° and 0·954 atm.[37] Ultrasonic waves have also been studied.[38, 39]

Melting and Boiling Point, Vapour Pressure and Latent Heat, Critical Constants

The most reliable data for heats of fusion and vaporization are those of Giauque and Johnston who find $0{\cdot}549_5$ and $3{\cdot}292_6$ kcal. mol.$^{-1}$, respectively.[4] The melting point was determined as 109·49° abs. and the boiling point as 121·36° abs. A survey of previous determinations is also given. These authors measured the vapour pressure of the solid and the liquid, and derive the following empirical equations, valid from 93° to 123° abs.

$$\text{Solid:} \qquad \log_{10} p\ (\text{cm.}) = \frac{-867}{T} + 0{\cdot}00076T + 9{\cdot}05125$$

$$\text{Liquid:} \qquad \log_{10} p\ (\text{cm.}) = \frac{-776}{T} - 0{\cdot}002364 + 8{\cdot}562128$$

These equations may be compared with the results of earlier workers,[30, 31] who deduced that the liquid must be strongly associated. More recently it has been suggested that liquid nitric oxide consists largely of dimeric $(NO)_2$ molecules, which would account for the abnormally high entropy of vaporization and the high and variable specific heat data.[32] This has been further discussed.[33]

Table V summarizes the values selected by the National Bureau of Standards.[29]

Table V.—Selected Values for the Thermodynamic Functions of Nitric Oxide, Associated with a Change of State

Process	Initial	Final	Pressure mm. mercury	T° abs.	ΔH kcal. mol.$^{-1}$	ΔS g.-cal. mol.$^{-1}$ deg.$^{-1}$
Fusion	solid	liquid	164·4	109·51	0·550	5·02
Vaporization	liquid	gas	760	121·39	3·293	27·13

The zero point energy of nitric oxide and the latent heat of sublimation at 0° abs. have been calculated.[34]

Despite the importance of critical data for computational purposes,[40, 41] the critical constants of nitric oxide are not well established, and the results given here must be treated with caution. The selected values of Pickering are −94°, 65 atm. and 0·52 g. c.c.$^{-1}$ for the critical temperature, pressure and density respectively.[42, 43]

Physical Properties Related to Properties of the Gas

The volume coefficient of expansion of nitric oxide is very close to the reciprocal of 273, and was found by Coppock and Whytlaw-Gray[44] to be $10^6\alpha^0_{12-48} = 3679$ deg.$^{-1}$

Compressibilities have been measured by several investigators,[45] two results for A at 0° being 0·00119[46] and 0·00112.[47] The compressibility of nitric oxide has been discussed from the point of view of the number of double molecules present in the gaseous phase.[48]

The low-pressure data of state of nitric oxide have been determined by Johnston and Weimer,[49] who give the following equation for the second virial coefficient in the range 120 to 300° abs.:

$$B = 20 + 5881{\cdot}5/T - 5{\cdot}7639 \times 10^6/T^2 + 8{\cdot}4301 \times 10^{10}/T^4 - 9{\cdot}2783 \times 10^{14}/T^6 \text{ c.c.mol.}^{-1}$$

The volumetric behaviour of nitric oxide at high pressures has also been examined.[50]

In the determination of the atomic weight of nitrogen, mass doublets have been found for nitric oxide–ethane[51] and nitric oxide–methyl (radical).[52]

The viscosity of gaseous nitric oxide has been measured[53–55] and discussed.[56–58] The results in Table VI are taken from the work of Johnston and McCloskey[59] who determined the viscosity by the rotating disc method.

Table VI.—Viscosity of Nitric Oxide as a Function of the Temperature ($g. cm.^{-1} sec.^{-1}$)

T° abs.	Viscosity × 10^7
120	843·6
160	1115·0
200	1371·2
240	1609·7
280	1837·6

These results may be compared with the data of Wobser and Müller[60] who find 1882×10^{-7} g. cm.$^{-1}$ sec.$^{-1}$ at 20°. The effect of magnetic fields on the viscosity has been studied.[61–63]

Thermal conductivities have been determined[64] and the results have been discussed.[57, 58, 65] The results given in Table VII are those of Johnston and Grilly,[66] taken from a smoothed curve.

Table VII.—Thermal Conductivities of Nitric Oxide as a Function of Temperature ($g.$-$cal. cm.^{-1} sec.^{-1} deg.^{-1}$)

T° abs.	Thermal Conductivity (× 10^5)
120	2·580
180	3·838
240	5·035
300	6·189
360	7·318
298·1	6·153
273·1	5·674

It has been reported that the thermal conductivity is affected by a magnetic field, although only a small change was observed.[67, 68, 69] Accommodation coefficients have been calculated from the data of Johnston and Grilly,[70] and the use of calibrated Pirani gauges with nitric oxide has been recommended.[71]

There appear to be no recent data on the diffusion of nitric oxide, although Andrussov has carried out several calculations on self-diffusion coefficients and on the interdiffusion of two gases.[57, 72, 73] Thermal separation ratios have also been calculated.[74]

PARAMAGNETISM

Nitric oxide contains an odd number of electrons and is therefore a paramagnetic gas. The magnetic susceptibility has been calculated by Van Vleck[75–77] yielding a result for the mass susceptibility (per g.) of $48{\cdot}3 \times 10^{-6}$ at room temperature. This value is in good agreement with the numerous experimental determinations which have been carried out.[78–86] The most recent result is that of Burris and Hause[86] who find a value of $47{\cdot}2 \times 10^{-6}$ for the mass susceptibility at 20°. The variation with temperature is also in agreement with theory, and is typified by the figures $49{\cdot}07 \times 10^{-6}$ at 292·1° abs. and $87{\cdot}32 \times 10^{-6}$ at 112·8° abs.[85, 169] The magnetic moment has also been determined by the Stern–Gerlach method.[87]

In view of the dimerization in the liquid and solid forms of nitric oxide, magnetic moment measurements are of considerable interest.[88] Smith and Johnston, in an investigation of the magnetic susceptibility of liquid nitric oxide over the temperature range 109 to 122° abs.,[89] found a temperature variation which could be interpreted in terms of an equilibrium between feebly magnetic dimeric molecules and a paramagnetic monomer. The degree of dissociation of the liquid varied from 2·7% at

110° abs. to 5·0% at 120° abs., and the heat of dissociation of the dimer was estimated to be 3·71 kcal. mol.$^{-1}$, which is in good agreement with the value obtained by Rice[32] from the entropy of vaporization of the liquid (3·91 kcal. mol.$^{-1}$). The susceptibility of the solid was similarly found to be extremely small.[90]

A further point of interest, with nitric oxide as with oxygen also, is the effect on the magnetic susceptibility of the formation of a clathrate compound. This has been studied for nitric oxide in the clathrate formed with quinol.[91] The value for nitric oxide at 17° was $51{\cdot}6 \times 10^{-6}$ (per g.). This work has been extended to low temperatures, and has indicated that from 10° to 300°K. the nitric oxide behaves as a free gas.[92]

The dipole moment of nitric oxide would be expected to be small and this is found to be true. The only results available are $0{\cdot}0_7$ debye (235–477° abs.)[93] and 0·16 debye (193–298° abs.).[94]

The magnetic birefringence of nitric oxide has been studied and values are given for the Cotton–Mouton constant.[95–97] This work has been discussed[98–100] and from measurements on the liquid it has been suggested that the proportion of dimeric molecules at −163° is 93%, while the proportion at −104° is 21%, reputedly in agreement with the fact that the liquid was observed to be blue at the higher temperature.[101] (The colour of liquid nitric oxide is in some doubt.)

The catalysis of the ortho-para hydrogen conversion by nitric oxide is due to the paramagnetic properties of the gas and this reaction has been studied.[102, 103] The continuous determination of nitric oxide, by virtue of its paramagnetism, has been suggested.[104]

The Structure of Nitric Oxide

The crystal structure of nitric oxide has been determined by Dulmage, Meyers and Lipscomb.[105, 106] The crystals are monoclinic of space group $P2_1/a$ and with two molecules of nitric oxide in the unit cell. The primitive translations are $a = 6{\cdot}68$, $b = 3{\cdot}96$, $c = 6{\cdot}55$ A., and $\beta = 127{\cdot}9°$. The solid consists of the dimer $(NO)_2$, and since all the peaks on the electron density map are of equal height, there are two possible orientations for it in the crystal, which accounts for the residual entropy. The averaged dimer is a rectangular planar molecule having a short edge of 1·12 A. and a longer edge of 2·40 A. Nitrous oxide has a dipole moment of 0·17 debye and a residual entropy of 0·90 g.-cal. mol.$^{-1}$ deg.$^{-1}$, while carbon dioxide with a dipole moment of 0·10 debye has a residual entropy of 1·12 g.-cal. mol.$^{-1}$ deg.$^{-1}$ In neither of these cases is the crystal completely disordered. The residual entropy of nitric oxide, however, in the dimeric molecule, is 1·50 g.-cal. deg.$^{-1}$ mol.$^{-1}$, suggesting complete randomization and a very low dipole. Lipscomb tends to favour the centrosymmetric model. The *X*-ray diffraction patterns of liquid nitric oxide have also been studied.[107] The infra-red and Raman data also show the spectra of the solid to be due exclusively to a dimer.[108] The nature of the bonding in the dimeric molecule has been discussed.[109]

The density obtained from the *X*-ray data is 1·46 g. c.c.$^{-1}$ at −175°. This may be compared with the experimental values of 1·57 g. c.c.$^{-1}$ at 20° abs.[110] and 1·556 g. c.c.$^{-1}$ at −195°.[111, 112] The density of the liquid has also been measured at various temperatures and a few results are shown in Table VIII.[113]

Table VIII.—The Density of Liquid Nitric Oxide (g. c.c.$^{-1}$)

$t°$	−163	−159·5	−156	−153·6
density g. c.c.$^{-1}$	1·332	1·306	1·277	1·227

Surface tension measurements were carried out at the same time.

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Miscellaneous Properties

The depolarization factor for nitric oxide has been found to be 0·0268.[114] This may be compared with an earlier value of 0·026.[115] The solid has been examined in polarized light.[116]

The motion of electrons in nitric oxide has been quite extensively studied,[117–136] and in a number of cases ionization potentials, generally lying between 9 and 9·5 ev., have been given. These compare favourably with two more recent determinations of 9·4 ev[137] and 9·23 ev.[138] The effect of alpha radiations,[139–141] protons[142] and neutrons[143] has been studied, as has the quenching of mercury resonance radiation.[144] Breakdown potentials in nitric oxide[145–147] and in nitric oxide–argon mixtures[148] have been investigated and the initial stages of spark formation in the gas have been studied in a Wilson cloud chamber.[149] The emission mechanism in a Tesla spark has been observed.[150]

Miscellaneous studies include polarographic reduction at a mercury electrode[151] where it has been shown that the half-wave potential is $-0{\cdot}5$ v.[152] and that the process involves one electron transfer.[153]

The absorption spectrum of liquid nitric oxide has been studied and it has been noted that the true colour of nitric oxide is blue and quite different from that of a solution of dinitrogen trioxide in nitrous oxide.[154] In studies of the spectrum of the gas it was found to decompose under high pressures.[155] Calculations on the emissivity of nitric oxide have been carried out[156, 157] and the dispersion of supersonic waves in gaseous mixtures of nitric oxide with carbon dioxide has been observed.[158]

Equilibrium constants have been calculated for various isotopic exchange reactions involving nitric oxide.[159]

Solution and Sorption Effects

In 1931 it was reported that nitric oxide dissolves in water to yield either nitrohydroxylamic acid or a compound of the same constitution.[160] This is probably incorrect. The solubility in water has been discussed,[161] and the rate of solution in air-free water at 22° has been given[162] as 0·0375 c.c. min^{-1} cm.$^{-2}$ or 0·000302 g.h.$^{-1}$ cm.$^{-2}$

The solubility of nitric oxide in sulphuric acid solutions, particularly those containing nitrosyl bisulphate, is of industrial importance. Table IX gives the solubility of nitric oxide in aqueous solutions of sulphuric acid at 20°[163] and Table X gives the solubility at 0°.[164]

Table IX.—Solubility of Nitric Oxide in Aqueous Solutions of Sulphuric Acid at 20°

% sulphuric acid (wt.)	c.c. nitric oxide (N.TP.) in 1 c.c of solvent
43·8	0.0134
54·6	0.0125
64·1	0.0096

Finally, the solubility in sulphuric acid solutions containing nitrosyl bisulphate is given in Table XI.[165]

The solubility in organic solvents has been discussed by Eley[166] and has been measured. Some results are shown in Tables XII, XIII and XIV.

Table X.—Solubility of Nitric Oxide in Aqueous Solutions of Sulphuric Acid at 0°

% sulphuric acid (wt.)	c.c. nitric oxide in 100 c.c. of solvent
0·0	7·38
8·8	6·9
18·2	5·9
28·0	5·4
38·6	4·9
48·0	4·0
58·7	3·3
70·8	3·0
78·0	3·2
88·3	3·5
92·4	4·6
95·0	7·1
95·9	7·7

Table XI.—Solubility of Nitric Oxide in Nitrosyl Bisulphate Solutions in Sulphuric Acid

% dinitrogen trioxide in the solvent	c.c. nitric oxide (at 18° and 760 mm.) per 1 c.c. of solvent	
	40°	70°
1·18	1·47	1·61
4·3	6·40	6·20
1·11	2·85	2·93
3·86	10·10	10·20

Table XII.—The Solubility of Nitric Oxide in Methanol.[167] *The Values given are the Ratio of the Molar Concentration in Solution to the Molar Concentration in the Gaseous Phase* (*Ostwald Coefficient*)

Temperature			
0°	10°	20°	30°
$0{\cdot}363_5$	$0{\cdot}362_2$	$0{\cdot}350_6$	0·347

Table XIII.—Solubility of Nitric Oxide in Carbon Tetrachloride, Benzene and Nitrobenzene[168] (*Ostwald coefficient*)

Benzene		Nitrobenzene		Carbon Tetrachloride	
t°		*t*°		*t*°	
8·8	0·275	20	0·189	8·8	0·339
14·6	0·284	40	0·190	19·6	0·345
24·6	0·300	60	0·193	34·6	0·375
34·6	0·318	90	0·188	—	—

Table XIV.—Solubility of Nitric Oxide in Toluene and Pentane (Ostwald coefficient)

n-Pentane		Toluene	
t°		*t*°	
0	0·260	19·8	0·127
−55·5	0·578	0	0·318
−76·1	0·746		
−77·8	1·54		

The solubility of nitric oxide in nitrosyl chloride is given in Table XV.[170]

Table XV.—Solubility of Nitric Oxide in Nitrosyl Chloride (Ostwald coefficient, β)

t°	β
−47·5	1·64
−53·1	1·16

It has been reported that the freezing point of water remains unchanged when nitric oxide is passed through it, and in several other solvents lowering of the freezing point was too small to be of any value in the determination of solubility.[171] In a later publication,[172] however, the concentration of a saturated solution of the gas (in g. per 100 g. of solvent) obtained from cryscopic determinations was given. The figures for nitric oxide are: in benzene 0·0235 (at 5·5°), in nitrobenzene 0·058 (5·2°), in *cyclo*hexane 0·337 (5·9°).

The surface tension of a newly formed gas–liquid surface has been studied for nitric oxide and water.[173]

The sorption of nitric oxide on metals,[174–178] charcoal,[179–182] sodium chloride,[183] potassium benzenesulphonate,[184] glass walls[185, 186] and silica gel[187, 188] has been studied. Addison and Barrer[189] found, however, that nitric oxide occluded by certain zeolites underwent a disproportionation reaction with relative ease:

$$4NO = N_2O + N_2O_3$$

This reaction occurred less readily on silica gel, while on charcoal there was a different reaction.

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REACTIONS OF NITRIC OXIDE

Third-Order Gas Phase Reactions

As has already been mentioned, several reactions of nitric oxide show abnormal kinetics in that they are of third order; these are summarized in the following scheme:

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO + Br_2 \rightarrow 2NOBr$$

$$2NO + Cl_2 \rightarrow 2NOCl$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

All these reactions are of second order with respect to nitric oxide and first order as to the other constituent. These reactions have been discussed in terms of the Wigner spin conservation rule, and it has been pointed out that the interaction of two doublets forms a singlet state.[1]

The reaction of nitric oxide with oxygen has already been discussed (see p. 162).

THE REACTION BETWEEN NITRIC OXIDE AND CHLORINE

The reaction of nitric oxide with chlorine was extensively studied around 1920, but there has not been any recent work. Welinsky and Taylor[2] found that the reaction is of third order over a wide concentration range, in agreement with Krauss and Saracini.[3] Earlier investigations were reported to show a variation of the rate constant with concentration,[4] and a mechanism involving $NOCl_2$ was proposed, but this conclusion has been seriously criticized.[2, 3] For example it has been stated that in many cases no account was taken of the decomposition of the product, nitrosyl chloride. Again, constants were in some cases calculated from zero time to time *t*, putting an undue emphasis on initial concentrations, while in other cases insufficient data were obtained to justify the conclusions.[2]

The constancy of the rate constant for the reaction between nitric oxide and chlorine is shown by data taken from the work of Welinsky and Taylor, Table XVI.

Table XVI.—Rate Constant for the Reaction between Nitric Oxide and Chlorine at 61·0°

Time (sec.)	k (c.c./mole)^2 sec.$^{-1}$
105	$3{\cdot}52 \times 10^7$
230	3·77
380	3·66
540	3·72
690	3·79
945	3·77
1230	3·64
1515	3·79
1915	3·74

The energy of activation steadily increases with temperature, the effect being more marked than that found for the oxidation of nitric oxide by oxygen.

Stoddart has thrown some doubt on the homogeneous nature of this reaction and has suggested that adsorption of nitrosyl chloride may cause such severe inhibition that reaction ceases.[5] The heterogeneous association of nitric oxide was stressed, as in the oxidation of nitric oxide by oxygen. It was subsequently found that there is an ageing effect so that the velocity of the reaction decreases from experiment to experiment, as well as during a single experiment. It was found that intensive drying prevents the inhibition.[6]

The equilibrium between nitric oxide, chlorine and nitrosyl chloride has been studied,[7, 8] as has the corresponding equilibrium involving bromine and nitrosyl bromide.[9] The equilibrium involving all the above constituents as well as bromine monochloride has been examined.[10]

Explosion limits have been studied in the system nitric oxide, hydrogen and chlorine,[11, 12] while the corresponding flames have also been examined.[13, 14] The results of the latter investigation were explained in terms of the non-branching chain mechanism shown below:

$$NO + Cl_2 \rightarrow NOCl + Cl$$
$$NOCl \rightarrow NO + Cl$$
$$Cl_2 \rightarrow Cl + Cl$$
$$Cl + H_2 \rightarrow HCl + H$$
$$H + Cl_2 \rightarrow HCl + Cl$$
$$Cl + NOCl \rightarrow NO + Cl_2$$
$$H + NOCl \rightarrow NO + HCl$$

Under the conditions of the experiment it was found that the first reaction provided the fastest initiation step.

THE REACTION BETWEEN NITRIC OXIDE AND HYDROGEN

The reaction between nitric oxide and hydrogen in clear fused-silica vessels has been found to be of third order at 826°.[15] At constant hydrogen concentration the rate of reaction is proportional to the square of the nitric oxide concentration, while at constant nitric oxide concentration the rate is nearly proportional to the hydrogen concentration. The divergence was thought to be due to a small surface effect which becomes less important at higher pressures. In subsequent work, however, this investigation was extended, and it was found that rate of the reaction between nitric oxide and hydrogen is approximately the same in packed and unpacked bulbs. Some of these results are shown in Fig. 3, where some data for nitric oxide and deuterium are also included.[16] There was no evidence of long chains, and the low pressure results were interpreted in terms of binary collision complexes of differing lives.

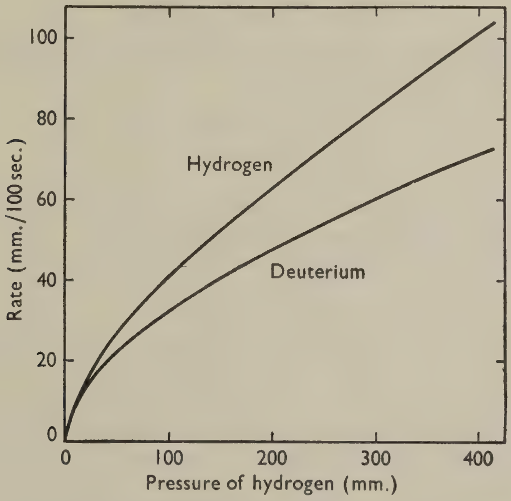

FIG. 3.—Variation of the initial rate of the reaction between nitric oxide and hydrogen or deuterium at constant nitric oxide concentration (30 mm. pressure)

The nitric oxide–hydrogen flame has been studied, and it has been suggested that the flame velocity may be governed by the bimolecular decomposition of nitric oxide.[17] The theoretical flame temperature for nitric oxide, initially at a temperature of 300°K. and at a pressure of one atm., is approximately 2650°K.

The catalytic reduction of nitric oxide by hydrogen has been examined. With rhodium as the catalyst the product is found to be ammonia,[18] whereas platinized platinum gives ammonia and hydroxylamine,[19] although it had previously been stated that a commercial catalyst produces only ammonia and nitrogen.[20] Rhenium[21] and platinum gauze[42] have also been examined, and in the reduction of nitric oxide in the presence of oxygen it has been reported that 98% of the hydrogen is oxidized to water, so that under these conditions nitric oxide is not reduced to ammonia on a platinum catalyst.[22]

The reaction between nitric oxide and hydrogen atoms has been examined by mercury sensitization of mixtures of nitric oxide with hydrogen. The products are nitrogen and water.[23] A mechanism based on HNO radicals was suggested to explain the experimental results.

The well-known catalysis of the ortho-para-hydrogen conversion by the paramagnetic nitric oxide molecule has been studied.[24] The collision yield agreed well with the theory of Wigner.

THE REACTION BETWEEN NITRIC OXIDE AND CARBON MONOXIDE

Musgrave and Hinshelwood found that the reaction between nitric oxide and carbon monoxide is partly heterogeneous.[25] The rate is proportional to the square of the nitric oxide concentration, but independent of the carbon monoxide concentration. The suggested reaction mechanism is:

$$CO + H_2O \rightarrow CO_2 + H_2$$
$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

the first reaction being fast and heterogeneous, while the second is homogeneous and could occur in the following way:

$$2NO + H_2 \rightarrow N_2O + H_2O$$
$$2N_2O \rightarrow 2N_2 + O_2$$

Recently this reaction has been examined over a higher temperature range (1380–1580°), and has been shown to be homogeneous.[26]

The reaction between nitric oxide and carbon monoxide,

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

is again of second order with respect to nitric oxide but of first order with respect to carbon monoxide.

It has been reported that in this reaction both nitric oxide and carbon monoxide, as well as oxygen atoms, are excited to start the reaction.[27] The drying of the two gases by cooling to −80° is said to result in explosion.[28]

Carbon monoxide may be removed from admixture with nitric oxide by passing the gases through a heated tube containing a platinum catalyst[29]; at 550° only 0·4% of carbon monoxide remained in the gas.

The explosive reaction of nitrous oxide with carbon monoxide has been studied in the presence of nitric oxide.[30, 31] It appears that nitric oxide inhibits the explosion. Injection of nitric oxide into the combustion zone in the carbon monoxide reaction with oxygen gives a yellow-green coloration, indicating atomic oxygen, where the mixture contained excess of oxygen.[32]

Reaction between Nitric Oxide and Carbon Disulphide

The explosive reaction of nitric oxide with carbon disulphide has been extensively studied, partly on account of the light emission during the explosion.[33–38] Some of the more interesting aspects of this system and the system with nitrous oxide are summarized in Figs. 4 and 5. It has been suggested that the light emission is due to free sulphur, which is deposited on the walls of the containing vessel.[38] From Fig. 5 it appears that for a binary mixture of carbon disulphide and nitric oxide, the best light emission would be obtained at a composition containing approximately 30% by volume of carbon disulphide. The rate of propagation for the mixture was about 3 m. per sec. at 14 cm. Hg total pressure and the dimensions of the vessel seemed to have little effect on this velocity.[39]

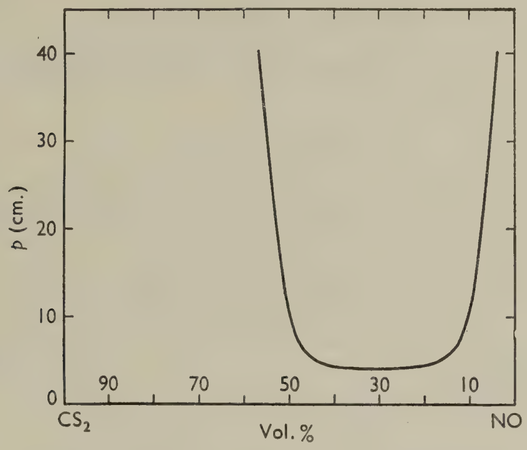

FIG. 4.—Explosion limits for CS_2—NO mixtures

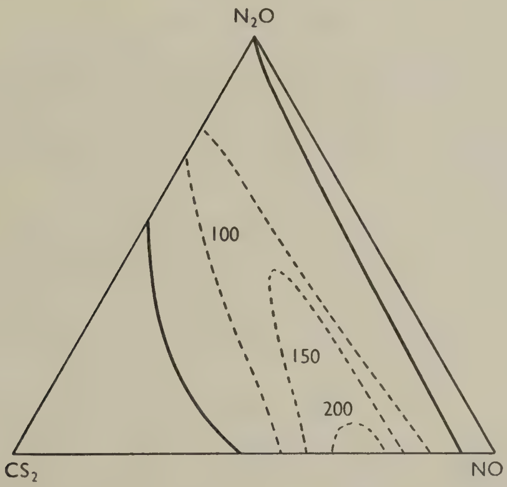

FIG. 5. Explosion limits for CS_2—NO—N_2O mixtures at 15 cm. total pressure. Pecked lines indicate equal light emission (iso-lumen-second lines)

Other Reactions of Nitric Oxide

The reaction between nitric oxide and ammonia has not been much studied and is not well understood.[40] It has been suggested that the reaction determining the flame velocity is faster than the decomposition of nitric oxide under the experimental conditions.[17] A study in 1954 indicated that in the temperature range 990°–1150°K. the initial pressure change is proportional to the ammonia concentration, but varies linearly with the square root of the partial pressure of the nitric oxide.[41] The experimental results were interpreted in terms of a reaction which is very rapid relatively to the rate of formation of the imine radical:

$$NH_2 + NO \rightarrow N_2 + H_2O$$

It was further suggested that the dehydrogenation of ammonia does not proceed via the reactions:

$$NH_3 \rightarrow NH_2 \rightarrow NH$$

The catalysed reaction on the surface of a platinum filament may be expressed by the equation:

$$2NH_3 + 3NO \rightarrow 2{\cdot}5N_2 + 3H_2O$$

Industrially this reaction is inhibited owing to the specific poisoning of the catalyst.[43]

The spark ignition of nitric oxide and *asym.*-dimethylhydrazine has been attributed to the heating of the system by the very exothermic reaction between nitric oxide and radicals.[44] The products of combustion are numerous.

The interaction of amine and N_2H_3 radicals with nitric oxide has been examined in a silica apparatus.[45] Mixtures of nitric oxide and ammonia or of nitric oxide and hydrazine were irradiated with a mercury arc. The results were interpreted in terms of the following equations:

$$NH_2 + NO \rightarrow N_2 + H_2O$$
$$N_2H_3 + NO \rightarrow N_2O + NH_3$$

It has been reported that if a mixture of nitric oxide and cyanogen is exposed to light of wave-length shorter than 360 mμ, the reaction occurring is:

$$4NO \rightarrow N_2 + 2NO_2$$

indicating that cyanogen may be a photosensitizer.[46] This system has been examined also in connection with its importance in the mechanism of combustion.[47]

The reaction between nitric oxide and phosphorus pentoxide is important as phosphorus pentoxide is frequently used as a drying agent for this gas. This does not introduce any impurity into the gaseous phase, as the glassy solid residue has the formula $P_2O_5{,}2NO$.[48]

Trisodium arsenite and nitric oxide react in the absence of a solvent to yield nitrous oxide and the arsenate.[49] If the nitric oxide is first dissolved in potassium sulphite solution, the reaction products are the same. This reaction has been further studied.[50]

The rather unusual reaction of nitric oxide with nitrogen trichloride at −150° may be represented by the equation:

$$NCl_3 + 3NO \rightarrow 2NOCl + N_2O + Cl$$

It is believed to take place in four steps.[51–53]

Active nitrogen decomposes nitric oxide, but not nitrous oxide,[54] and it has been found that the rapid reaction between nitric oxide and nitryl chloride is homogeneous and first order with respect to each constituent.[55]

Gaseous nitric oxide and hydrogen sulphide react at temperatures between 28° and 100° to yield sulphur, water and nitrogen.[56] The reaction is catalysed by silica gel or glass wool. Later it was suggested[57] that perfectly dry nitric oxide and hydrogen sulphide do not react, and that in the presence of water the velocity depends on the ratio of the pressures of the nitric oxide and the hydrogen sulphide.

Where the hydrogen sulphide is in solution in water the products are ammonium thiosulphate, ammonium nitrite, sulphur, nitrous oxide and nitrogen.[58] With ammonium sulphide solution, ammonium polysulphides are formed and nitrous oxide and nitrogen are evolved. More recently, however, the following reactions[59] have been suggested:

$$S^{--} + 2NO + H_2O \rightarrow S + N_2O + 2OH^-$$
$$S + 6NO + 2OH^- \rightarrow [(NO)_2SO_3]^{--} + 2N_2O + H_2O$$

The reactions of nitric oxide with the oxides and oxy-acids of sulphur are complex, When nitric oxide is led into molten sulphur trioxide at 60° a vigorous reaction ensues.[60] The product fuses completely at 200°, and when distilled at 270° yields a condensate, solid and very hygroscopic, having the formula $(SO_3)_2NO$. The same compound is formed from dry sulphur dioxide and nitrogen dioxide above 160°. With sulphur dioxide the following reactions are suggested[61]:

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$
$$SO_2 + NO + O_2 \rightarrow SO_3 + NO_2$$

although in the absence of water the compounds do not react. These reactions warrant further study.

The reduction of nitric oxide by sulphur dioxide in the presence of water yields nitrous oxide. The reaction mixture contains dilute sulphuric acid, ferrous sulphate, dilute nitric acid and sodium sulphite.[62] The reduction of nitric oxide to nitrous oxide is a source of loss in the chamber process for the production of sulphuric acid, and this loss has been studied. Nitrogen may also be formed during the reduction.[63] Raschig found that the action of nitric oxide on 40% potassium sulphate solution in the absence of air eventually yields needle shaped crystals of the formula $K_2N_2SO_5$,[64] while the corresponding sodium salt is formulated as Na_2SO_3,N_2O_2.[65] It is formed by the action of nitric oxide on sodium dithionite:

$$Na_2S_2O_4 + 6NO + 2NaOH \rightarrow Na_2SO_3,N_2O_2 + Na_2SO_4 + 2N_2O + H_2O$$

Decomposition of the potassium salt in aqueous solution leads to the formation of nitrous oxide,[66] while with the dry salt both nitrous and nitric oxides are formed. In view of the smooth decomposition with dilute sulphuric acid, this is suggested as a suitable method for the preparation of 100% nitrous oxide.[66]

Kinetic measurements have been made on the reduction of nitric oxide by sulphurous acid and the following scheme is suggested[67]:

$$H_2SO_3 + NO \rightarrow H_2SO_3NO$$
$$2H_2SO_3NO \rightarrow H_2SO_3(NO)_2 + H_2SO_3$$
$$H_2SO_3(NO)_2 \rightarrow H_2SO_4 + N_2O$$

In the synthesis of the salt having the empirical composition

$$K_3[NONi(S_2O_3)_2],2H_2O$$

it is suggested that reductions of the following type occur[68]:

$$2NO + 2S_2O_3^{--} \rightarrow 2NO^- + S_4O_6^{--}$$
$$[Ni(S_2O_3)_3]^{----} + NO \rightarrow [ONNi(S_2O_3)_2]^{---} + 0{\cdot}5S_4O_6^{--}$$

The possible side reactions have also been discussed.

The effect of nitric oxide on the decomposition of disulphur hexafluoride has been examined,[69] and the absorption of nitric oxide by an alkaline solution of $(KSO_3)_2NO$ has been noted.[90]

The action of nitric oxide on metallic carbonyls is well known and may be considered here primarily from a chronological viewpoint. Nitric oxide was found to give a blue compound with nickel carbonyl and a cherry red liquid $[Co(CO)_3NO]$ boiling at 78·6° with cobalt carbonyl.[70] Reaction with iron enneacarbonyl at 70–85° gave a red liquid, $[FeNO,3Fe(CO)_5]$. The work on nickel carbonyl has not been substantiated, and three papers which appeared in 1936–1937 do not seem to be in agreement.[71–73] It may, however, be said with some certainty that the reaction is not a simple one and may involve the reaction of nitric oxide with the decomposition products of nickel carbonyl. It appears that the compounds $[CoNO(CO)_3]$ and $[Fe(NO)_2(CO)_2]$ are well established, and it is of course tempting to postulate the series $[Ni(CO)_4]$, $[CoNO(CO)_3]$, $[Fe(NO)_2(CO)_2]$, $[Mn(NO)_3CO]$, $[Cr(NO)_4]$,[72, 74] although the other members are not known.

The nitrosyl compounds of ruthenium are very numerous. The chemical equivalence of nitric oxide and carbon monoxide has been discussed in connection with the reaction between nitric oxide and $RhCl_2.RhO.3CO$, yielding $RhCl_2.RhO.3NO$.[75]

The reaction of nitric oxide with a ferrous salt in the presence of ethyl mercaptan has been discussed,[76–78] but a much better known and extensively studied reaction is that with ferrous salts in aqueous solution. By expressing the equilibrium constant for the reaction:

$$FeSO_4 + NO \rightleftharpoons FeSO_4.NO$$

in the form $K = P[(22{\cdot}4 - V)/V]$, where P is the pressure of the nitric oxide in mm. of mercury and V is the volume of nitric oxide (in litres) bound by one mole of ferrous salt, it was found that the curve of log K against the reciprocal of the absolute temperature is linear.[79] The reaction is exothermic and at 100° the compound would be almost entirely dissociated. At 90° the ferrous salt is oxidized by the nitric oxide. Subsequently the absorption by ferrous selenate was discussed and it was noted that the corresponding equilibrium constant was smaller than that for the sulphate.[80] If cold absolute alcohol saturated with nitric oxide is added to a cold aqueous solution of ferrous selenate, after about two hours crystals of the formula $FeSeO_4.NO,4H_2O$ separate.

The absorption spectra of alcoholic solutions of ferrous chloride containing nitric oxide have been studied, and it has been found that the band shifts towards the blue and becomes broader in aqueous alcoholic solutions.[81] In the presence of nitric oxide, the spectra of dilute alcoholic solutions of ferrous chloride are practically identical with those of ferrous sulphate in dilute acid. The solubility of nitric oxide in concentrated phosphoric acid solutions of $FeHPO_4$ was measured. These results have been discussed in terms of two compounds of the type $FeSO_4.NO$, one being brown and the other red.

The absorption of nitric oxide in aqueous solutions of ferrous sulphate has been measured recently,[82] as has the rate of solution.[83]

The oxidation of various ferrous compounds by nitric oxide has been studied. For example, when a solution of ferrous sulphate at 0° is saturated with nitric oxide and then an alkali hydroxide is added, the initial black precipitate rapidly becomes red and a gas is evolved.[84] This gas is found to be a mixture of nitrogen and nitrous oxide, while the solid contains ferric iron. More generally it is found that certain ferrous salts of weak acids which are readily oxidized reduce nitric oxide to nitrous oxide.[85] It has also been stated, however, that nitric oxide is not reduced by ferrous sulphate, pyrophosphate or tartrate.[86]

In connection with the removal of impurities from gas by iron compounds, black 'sodium ferroheptanitrosyl sulphide' has been isolated.[87] It has also been pointed out that Roussin's black salt is more stable than the red salt, but it was not possible to identify this compound[88] in iron compounds which had been used in the purification of dry gases.

An attempt has been made to classify the iron compounds of nitric oxide in one uniform system.[89]

The ion $N_2O_3^+$ has been shown to be formed either from nitric oxide and the nitronium ion or from nitrogen dioxide and the nitrosonium ion.[91] Similarly, blue solutions of $N_2O_2^+$ compounds may be prepared in which nitric oxide may be regarded as acting as a Lewis base. For example $N_2O_2HSO_4$ may be prepared from nitrosonium bisulphate by the action of nitric oxide under pressure. Both the solid and the solutions are unstable.[92] It is interesting that nitrosyl chloride does not give

N_2O_2Cl up to 20 atm. Nevertheless solutions of nitric oxide in nitrosyl chloride have a dark brown colour.

The above comments are of interest in connection with the so-called red hydrochloric acid. It has been found that mixtures of nitric oxide and hydrogen chloride condense at temperatures in the region of 120–130° abs. to produce a deep blue liquid containing a complex of the possible composition NOHCl. The solution has conductivity greater than 10^{-3} reciprocal ohms.[93] On the other hand it has been reported that in the presence of small quantities of nitric oxide hydrochloric acid has a red colour,[94] while in the absence of nitric oxide no red colour could be observed. This is contrary to some recent work which shows that when anhydrous hydrogen chloride is rapidly frozen with liquid nitrogen a red colour is produced. A spectrographic analysis showed less than 0·1% of impurities of mass number 6–100.[95] It is suggested that although 10^{-4} to 10^{-5} mole fraction of nitric oxide intensifies the colour, the colour is due to imperfections in the crystals of solid hydrogen chloride. It has also been suggested that pure nitric oxide free from higher oxides does not form NOHCl.[96] It appears possible that the ion $N_2O_2^+$ may be responsible for the colour, but alternatively it seems reasonable to think also in terms of HNO^+.

The reaction between nitric oxide and mercury in the radiation from a mercury lamp is believed to lead to the production of nitrogen dioxide which could react further with the mercury.[97]

The reaction of nitric oxide with sodium atoms is not chemi-luminescent and appears to be of third order.[98, 99] When the bulk metal is heated in nitrogen containing about 20% of nitric oxide it becomes blue-green at about 65° and begins to react at 160–170°, producing a solid, $(NaNO)_x$, which dissolves in water to yield an alkaline solution and nitrous oxide.[100] A similar reaction has been observed with sodium in liquid ammonia.

The reaction of nitric oxide with various metals has been examined.[101]

The reaction between sodium oxide (Na_2O) and nitric oxide at 100° gives initially Na_2NO_2 which then decomposes according to the equation:

$$4Na_2NO_2 \rightarrow 2Na_2O + 2NaNO_2 + Na_2N_2O_2$$ [102]

The reaction with alkali metal hydroxides is of considerable importance as these are frequently used to remove higher oxides of nitrogen from nitric oxide. With aqueous solutions of potassium hydroxide some nitrogen is formed.[103] With solid potassium, sodium, cæsium, lithium, calcium, strontium and barium hydroxides at room temperature both nitrous oxide and nitrogen are formed[104]:

$$4NO + 2MOH \rightarrow N_2O + 2MNO_2 + H_2O$$
$$6NO + 4MOH \rightarrow N_2 + 4MNO_2 + 2H_2O$$

The rate of reaction increases with increasing atomic weight of the metal and with increasing surface area. The reaction with calcium oxide has also been studied.[119]

Lithium aluminium hydride is soluble in ether, and when a stream of nitric oxide is passed through this solution hyponitrous acid is obtained.[105] The etherate of aluminium triethyl gave, with nitric oxide, a product believed to hydrolyse to EtN(NO)OH.[106] The pyrolysis of cadmium dimethyl and of tetramethyl tin in the presence of nitric oxide has been studied.[107, 108]

It is reported that 'bis(disalicylidene-ethylenediamine)-*n*-aquo-dicobalt' absorbs one molecule of nitric oxide per cobalt atom, to form a very stable product.[109]

Miscellaneous studies include the preparation of hydrogen cyanide from nitric oxide and hydrocarbons,[110–112] the combustion of charcoal in nitric oxide,[113] the effect of nitric oxide on the reduction of ferric oxide by hydrogen[114] and, in connection with the supposed autocatalytic action of nitric oxide, the effect of stirring on the reaction of metals with nitric acid.[115]

The mechanism of the absorption of oxides of nitrogen by lead dioxide in microcombustions has been examined and the results have been interpreted in terms of the equation:

$$2NO+2PbO_2 = Pb(NO_2)_2,PbO+\tfrac{1}{2}O_2$$[116]

The reaction of nitric oxide with vanadous salts apparently involves the initial production of a complex $[V(NO)]^{++}$ which is rapidly reduced by excess of vanadous ion.[117] In the presence of dialkyl dithiocarbamates it is possible to isolate the extremely unstable diamagnetic compound $(NO)V[SC(S)NR_2]_2$.

Nitric oxide can be oxidized to dinitrogen pentoxide by means of ozone in the silent electric discharge.[118] The oxidation by iodine pentoxide is also of interest and may occur in any of the following ways[120]:

$$10NO+2I_2O_5 = 2I_2+5N_2O_4$$

followed by

$$5N_2O_4+I_2O_5 = I_2+5N_2O_5$$

or

$$10NO+3I_2O_5 = 3I_2+5N_2O_5$$

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SECTION XXVI

DINITROGEN TRIOXIDE

BY I. R. BEATTIE

Preparation

The usual methods of preparation of dinitrogen trioxide involve the reduction of nitric acid, or the action of concentrated sulphuric acid on a nitrite. It has been observed that a deep blue colour is developed when pieces of aluminium are suspended in nitric acid.[30] There is no doubt, however, that for the purposes of accurate work the only satisfactory method for preparing dinitrogen trioxide is the reaction of equimolar proportions of nitrogen dioxide and nitric oxide, or alternatively of nitric oxide with the requisite quantity of oxygen. It appears that the rather obvious methods of preparation involving the interaction of a nitrosyl compound with a nitrite have not been examined.

Physical Properties

Dinitrogen trioxide might with some justification be termed the Cinderella of the nitrogen oxides. None of its physical properties can be said to be known with any degree of certainty; the infra-red data have led only to a probable structure for the molecule, while the *X*-ray data have not yielded any satisfactory three-dimensional analysis. The range of stability of the compound is not known. The treatment here of this oxide therefore differs from that of the other oxides in that it is impossible to give a comparable analysis of available data.

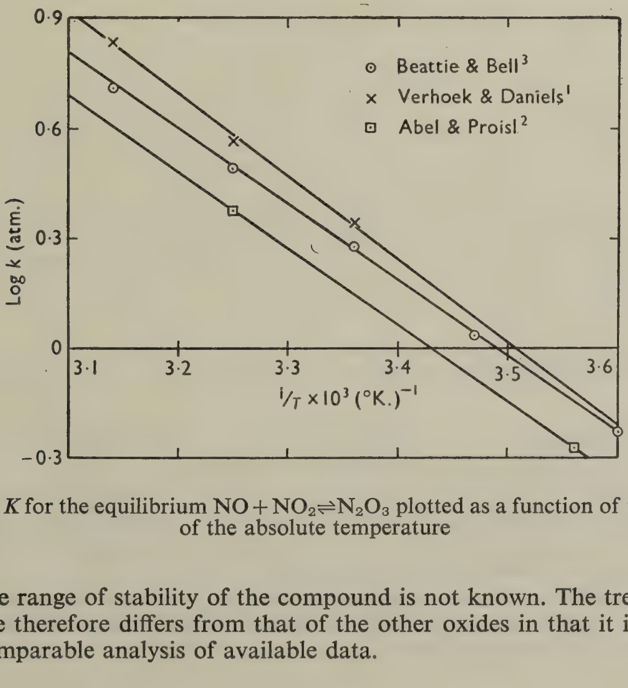


FIG. 1.—Log K for the equilibrium $NO + NO_2 \rightleftharpoons N_2O_3$ plotted as a function of the reciprocal of the absolute temperature

The stability of dinitrogen trioxide in the gaseous phase has been extensively studied, but the results of various investigators are not fully in agreement. By studying the equilibrium:

$$NO + NO_2 \rightleftharpoons N_2O_3$$

over a range of concentrations it is possible to obtain thermodynamic equilibrium constants by extrapolation to zero pressure.[1, 2, 3] These results are all shown on the same graph in Fig. 1. The values obtained for the heat of reaction are 10·300[1], 9·600[2] and 9·527 ± 0·096[3] kcal. mole^{-1}. The most recent workers found the entropy change for the reaction to be 33·25 ± 0·35 g.-cal. mole^{-1} deg.$^{-1}$.

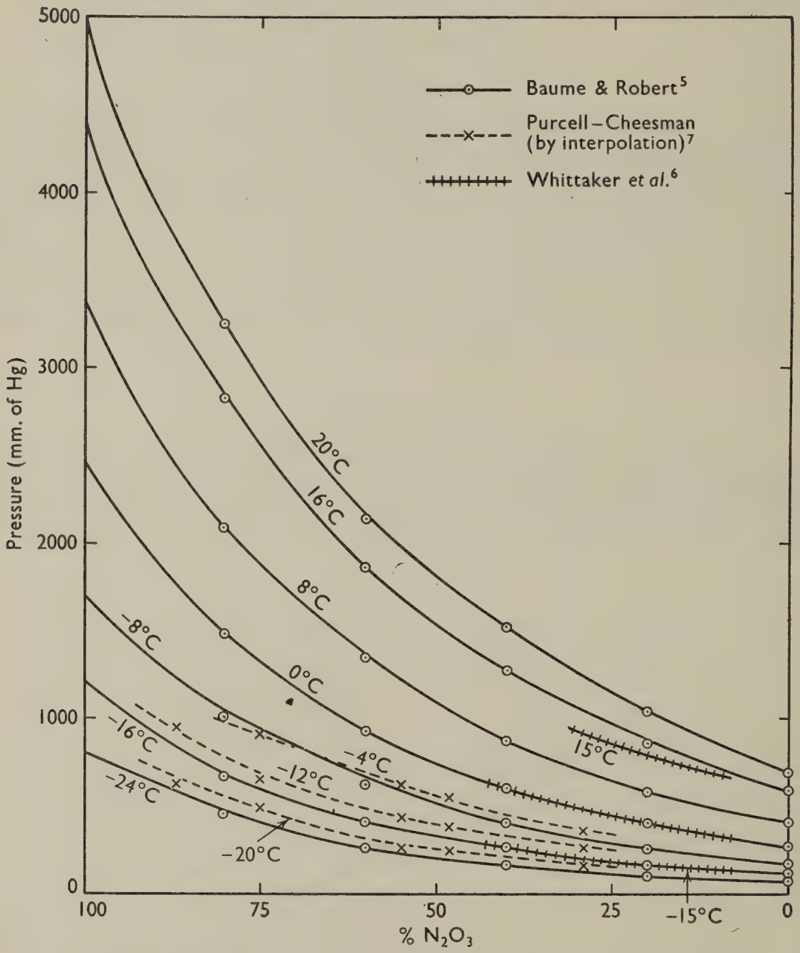


FIG. 2.—Vapour pressure–composition diagram for dinitrogen trioxide

Physical measurements on liquid dinitrogen trioxide are lacking. A spectrographic study of the solution of dinitrogen trioxide in toluene[4] showed that at −50° there is an absorption maximum at about 500 mμ. It has been suggested that at −50° dinitrogen trioxide is less than 6% dissociated.[4, 35]

Vapour pressures over the liquid, and over various mixtures with dinitrogen tetroxide, have been determined and the individual determinations are in reasonable agreement. Fig. 2 compares the low pressure data of three investigators.[5, 6, 7] This work has been extended to higher pressures[8] and the results of this investigation are shown in Table I.

Table I.—Vapour Pressure of Mixtures of Nitric Oxide and Nitrogen Dioxide (mm. Hg)

Weight % N_2O_3	20°	25°	30°	35°	40°	45°	50°
18·8	1010	1180	1430	1750	2130	—	—
43·6	1620	1860	2210	2650	3170	3760	4420
71·6	2740	3210	3800	4500	5300	6190	7170
98·4	4860	5700	6690	7820	9080	10460	11960

A more recent examination of the volumetric and phase behaviour of mixtures of nitric oxide and nitrogen dioxide contains data up to a temperature of 340°F., and seems to be primarily of technical importance.[9]

The phase diagram of the system nitrogen dioxide and dinitrogen trioxide is well known at the nitrogen dioxide-rich end. In the vicinity of dinitrogen trioxide there is, however, no reliable published work. Fig. 3 contains the relevant data,[5, 6] and includes some unpublished work by Beattie, Bell and Lewis.[10] The experiments in the region of the dinitrogen trioxide composition are being repeated.

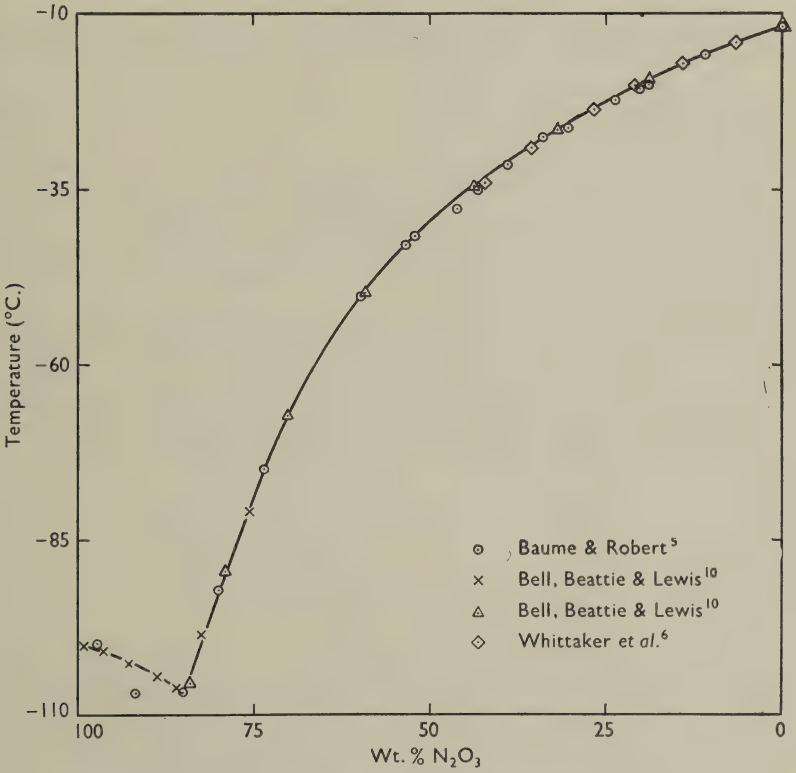


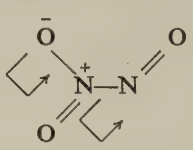
FIG. 3.—Freezing point diagram for the system NO_2—N_2O_3

In connection with the stability of dinitrogen trioxide some experiments on the intensive drying of this compound are of interest. Initially it was thought that intensively dried dinitrogen trioxide does not dissociate at all readily. This work was not confirmed,[11] and Stoddart has since shown that the results are invalidated by the fact that nitrogen dioxide and the drying agent (phosphoric oxide) react with one another.[12, 13]

The binary system dinitrogen trioxide and water has been studied,[14] as have the rapid gas phase reaction between nitric oxide, nitrogen dioxide and water[15] and the absorption spectrum of the gaseous mixture.[24]

The reaction between ^{14}NO and $^{15}NO_2$ has been studied in the gas phase at −35° and at a total pressure of 2·5 cm. Hg.[16] The rate of reaction is found to be extremely rapid, the lower limit of the rate constant being 10^6 c.c. mole^{-1} sec.$^{-1}$. From these results it is suggested that the energy of activation for the formation of dinitrogen trioxide is less than 1 kcal. mole^{-1}. It has also been stated that this exchange proves the existence of an oxygen bridge between both nitrogen atoms, but this is almost certainly incorrect.

Ingold and Ingold[17] suggest that the physical and chemical properties of dinitrogen trioxide are best represented by the structure



It has also been noted that dinitrogen trioxide may be considered as the nitrosyl compound, $(NO)_2O$.[18]

The crystallographic study of dinitrogen trioxide has been carried out by Lipscomb and Reed.[19, 20] The unit cell at −115° is tetragonal, with a = 16·4 A. and c = 8·86 A., and contains 32 molecules. The probable space group is $D_4^{10} - I\,4_12$. The three-dimensional analysis could not be solved and it is suggested that the structure is disordered. This is further borne out by a marked transition at −125°.

In many ways the most convincing evidence for the structure of dinitrogen trioxide is obtained from the infra-red data on mixtures of nitric oxide and nitrogen dioxide.[21] This evidence is strongly in favour of a nitrogen–nitrogen bond, similar to that found in dinitrogen tetroxide.

The ultra-violet spectrum of mixtures of nitric oxide and nitrogen dioxide has been reported to be anomalous, owing to the formation of dinitrogen trioxide. For example, with considerable amounts of nitric oxide containing small amounts of nitrogen dioxide a continuous absorption was found in the ultra-violet, obscuring the absorption of nitric oxide and also that of nitrogen dioxide below 2500 A.[22] Some of the more recent results are shown in the approximate curve of Fig. 4.[23]

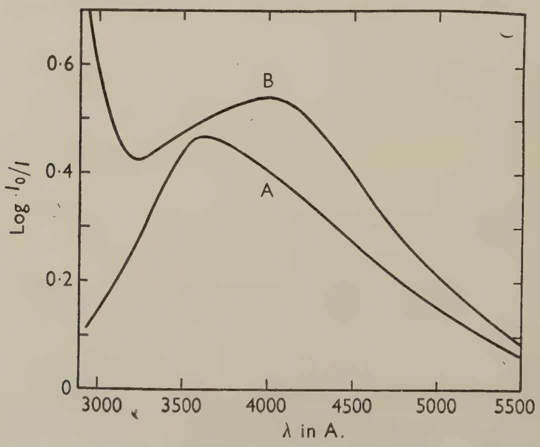


FIG. 4.—Absorption spectra of gas mixtures. A, 7·29 mm. NO plus excess O_2 to 1 atm. B, 3·63 mm. O_2 plus excess NO to 1 atm. (10 cm. cell)

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Miscellaneous measurements on what the authors term dinitrogen trioxide include the magnetic susceptibility ($-0{\cdot}21 \times 10^{-6}$),[24, 25] the density[26] (1·782 g. c.c.$^{-1}$ at $-195°$)[27, 28] and the freezing-point lowering of stannic chloride by the addition of dinitrogen trioxide,[29] which is found to be negligible. From the phase diagram of the system dinitrogen trioxide–nitrogen dioxide[3] it appears that the freezing point of dinitrogen trioxide is approximately $-100°$. In view of the dissociation of dinitrogen trioxide at higher temperatures it is clearly impossible to give a true boiling point for the liquid, and figures quoted merely refer to the temperature at which the total vapour pressure over the mixture is equal to 1 atm.

Reactions

In considering studies of the reactions of dinitrogen trioxide with various reagents it must be stressed that in general the purity of the dinitrogen trioxide has not been known, and the reactant has really been a mixture.

The reaction of mixtures of nitric oxide and oxygen with mercury has been examined, and it has been shown that both nitrate and nitrite are produced.[31] Miscellaneous studies include the reactions with phosphorus trichloride[32] giving a variety of products, with nickel carbonyl[33] to yield a brown-red solid, and with potassium iodide[34] to form iodine. The complex of dinitrogen trioxide with boron trifluoride is said to be a colourless crystalline solid, suitable for carrying out organic reactions.[35]

The interaction of dinitrogen trioxide with certain metallic oxides has been suggested as a means of preparing anhydrous nitrates.[36]

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SECTION XXVII

NITROGEN DIOXIDE AND DINITROGEN TETROXIDE

BY I. R. BEATTIE

THE PREPARATION OF THE MIXTURE OF NITROGEN DIOXIDE AND DINITROGEN TETROXIDE

The preparation of nitrogen dioxide usually involves the decomposition of a heavy metal nitrate or the reduction or decomposition of nitric acid. The main interest in the preparation has been improvement in the techniques of handling otherwise well established reactions. A simple glass apparatus for the preparation of small quantities of nitrogen dioxide has been described.[1] The preparation of nitric oxide, or mixtures of nitrogen dioxide and nitric oxide, followed by oxidation of the product to yield only nitrogen dioxide has also been described.[2] A recent paper deals with the purification of nitric oxide obtained from cylinders, followed by its oxidation to nitrogen dioxide.[3] The main impurities in the original nitric oxide are listed. Silver nitrate reacts quantitatively with nitrosyl chloride to yield nitrogen dioxide.[9]

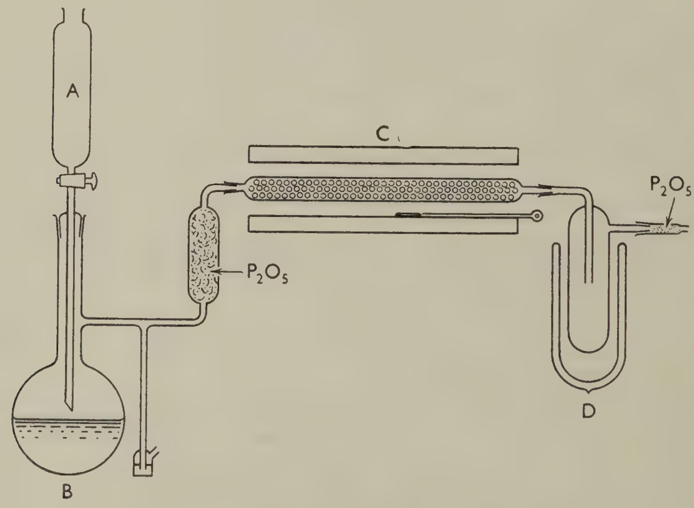

FIG. 1.—Apparatus for the preparation of nitrogen dioxide

A regular flow of nitrogen dioxide may be obtained by allowing a steady stream of sulphur dioxide to flow through concentrated nitric acid at a temperature of 80°.[4] An alternative method for obtaining nitrogen dioxide from nitric acid is to treat the fuming acid with phosphoric oxide at a low temperature and then apply heat to drive off a mixture of nitrogen dioxide and dinitrogen pentoxide, which is then completely decomposed to nitrogen dioxide by passage through a heated tube.[5] This method has recently been described in some detail.[6] The purification of nitrogen dioxide from nitric oxide requires elaborate manipulation. The reaction flask B (Fig. 1) has a capacity of about 750 ml. and contains initially 250 g. of phosphoric oxide.

The dropping funnel *A*, fitted by means of a ground joint, contains 105 ml. of colourless fuming nitric acid more concentrated than 95%. (The proportions of the reactants are 0·88 mole of phosphoric oxide to 2·25 mole of nitric acid.) The furnace *C* is held at 260°, and the nitric acid is then added drop by drop to the flask *B*, at such a rate that acid is not carried over into the furnace tube. It is advisable to ensure that the inlet tube for the nitric acid cannot become blocked during the addition. After about twenty minutes the apparatus will have been flushed out and nitrogen dioxide may be collected by cooling trap *D* with solid carbon dioxide. The reaction must be stopped after the addition of 100 ml. of nitric acid.

To purify the product of this reaction the apparatus shown in Fig. 2 may be used. The impure nitrogen dioxide held in the trap *B* is allowed to melt and then to distil into *C* through a phosphoric oxide trap in a stream of oxygen obtained from the liquid boiling in *A*.

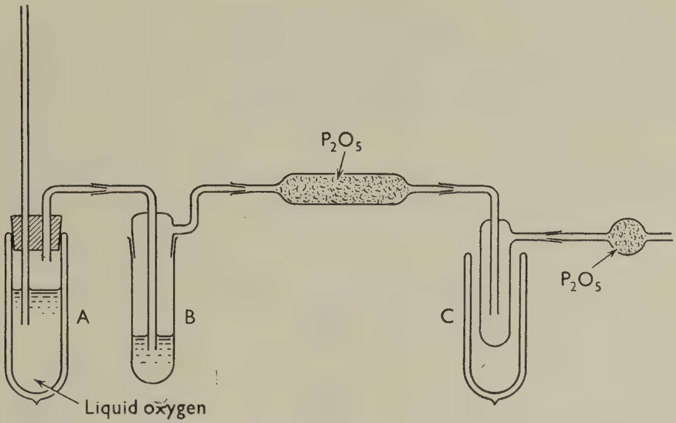

FIG. 2.—Apparatus for the purification of nitrogen dioxide

The last preparative method to be considered is the most popular, and is that favoured by the author; it has been in use for a considerable time,[7] and this description is taken from the work of Addison.[8] Lead nitrate, previously dried for at least two hours, is heated in a steel tube, to about 400°, batches of about 250 g. being suitable for laboratory preparation. The evolved gases are passed through phosphoric oxide to act as a drying agent, a tube some 30 cm. long and 2 cm. in diameter being suitable if packed loosely with phosphoric oxide using glass wool as a spacer. The gaseous nitrogen dioxide is condensed in a solid carbon dioxide bath and redistilled through phosphoric oxide.

Where a product of high purity is required it is preferable to carry out this reaction in a vacuum system. The nitrogen dioxide may then be purified from any dinitrogen trioxide or nitric oxide by several distillations in an atmosphere of oxygen (usually about 0·5 atm.) followed by several sublimations in a vacuum. The product may then be sealed into ampoules. It is useful to note that nitrogen dioxide readily attacks most tap greases. Silicone greases appear to be fairly resistant but are not pleasant to use or to remove subsequently. The newer halogenated greases are very much less reactive, but nitrogen dioxide is readily soluble in them. Rubber connections are inadmissible and calcium chloride is not a suitable drying agent as it may react to produce nitrosyl chloride.

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PHYSICAL PROPERTIES OF NITROGEN DIOXIDE AND DINITROGEN TETROXIDE

The system $NO_2-N_2O_4$ has been discussed in recent reviews.[1, 1a]

Thermodynamic Functions

Calculations of thermodynamic functions of nitrogen dioxide and dinitrogen tetroxide have been made by several investigators.[1b–6] The most recent data for nitrogen dioxide,[6] calculated from spectroscopic work, are given in Table I.

Table I.—Thermodynamic Functions of Nitrogen Dioxide (in g.-cal. mole^{-1} deg.$^{-1}$)

T°K.	C°_{p}	S°
100	7·95	48·35
200	8·23	53·92
250	8·53	55·78
275	8·70	56·60
298·16	8·87	57·32
300	8·89	57·37
325	9·07	58·09
350	9·27	58·77

These results may be compared with those of Giauque and Kemp[3] who give a value of 57·47 units as the entropy at 298·1°K., only 0·15 units higher than the value given in the above table for the same temperature. Another series of values, including data for dinitrogen tetroxide, is given in Table II, which is taken from the work of Kobe and Pennington.[4]

Table II.—Heat Capacities of Nitrogen Dioxide and Dinitrogen Tetroxide (in g.-cal. mole^{-1} deg.$^{-1}$)

t°	Nitrogen dioxide	Dinitrogen tetroxide
0	8·66	18·1
25	8·87	18·9
100	9·46	20·8

Giauque and Kemp[3] have calculated the entropy of a mixture of nitrogen dioxide and dinitrogen tetroxide at the boiling point as 80·62 g.-cal. mole^{-1} deg.$^{-1}$ (where the total quantity of material present is the molecular weight of dinitrogen tetroxide in g.). They calculated the entropy of dinitrogen tetroxide at the boiling point (294·25°K.) to be 72·5 g.-cal. mole^{-1} deg.$^{-1}$.

The values selected by the National Bureau of Standards are shown in Table III.[7]

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Table III.—Selected Values for the Thermodynamic Properties of Nitrogen Dioxide and Dinitrogen Tetroxide at 298·16°K.

	$\Delta H°$ kcal. mole^{-1}	$S°$ g.-cal. mole^{-1} deg.$^{-1}$	$C_p°$ g.-cal. mole^{-1} deg.$^{-1}$
nitrogen dioxide	8·091	57·47	9·06
dinitrogen tetroxide	2·309	72·73	18·90

The specific heat of a mixture of nitrogen dioxide and dinitrogen tetroxide has been measured over the range 34° to 160° and it has been suggested that the heat capacities of the two gases must be about the same.[8]

The melting and boiling points of the nitrogen dioxide and dinitrogen tetroxide system as determined by previous workers are tabulated by Giauque and Kemp.[3] These authors give the freezing point of dinitrogen tetroxide as 261·90°K., and the boiling point of the mixture as 294·25°K. The heat of vaporization at the boiling point was found to be 9·110 kcal. mole^{-1}. Correspondingly, the heat of fusion at the melting point is 3·502 kcal. mole^{-1}. A subsequent determination of the heat of vaporization has been reported.[9]

Vapour pressure data for the mixture of nitrogen dioxide and dinitrogen tetroxide have been represented by the following equations[3]:

Liquid, 261·90° to 294·9° K.:

$$\log p \text{ (int. cm. mercury)} = -1753{\cdot}000/T + 8{\cdot}00436 - 11{\cdot}8078 \times 10^{-4}T + 2{\cdot}0954 \times 10^{-6}T^2$$

Solid, 240·3° to 261·90° K.:

$$\log p \text{ (int. cm. mercury)} = -2460{\cdot}000/T + 9{\cdot}58149 + 7{\cdot}61700 \times 10^{-3}T - 1{\cdot}51335 \times 10^{-5}T^2$$

These results may be compared with those of other workers.[10–12] The supposed effect of intensive drying on the boiling point of nitrogen dioxide[15] must be viewed with some caution since nitrogen dioxide reacts with phosphoric oxide according to the equation[16]:

$$P_2O_5 + N_2O_4 = P_2O_5{,}2NO + O_2$$

Selected values for the thermodynamic functions of dinitrogen tetroxide associated with change of state, chosen by the National Bureau of Standards, are shown in Table IV.

Table IV.—Selected Values for Thermodynamic Functions of Dinitrogen Tetroxide, Associated with Change of State

	Pressure mm. Hg	Temperature °K.	ΔH kcal. mole^{-1}	ΔS g.-cal. mole^{-1} deg.$^{-1}$
Fusion	139·78	261·96	3·502	13·37
Vaporization	760	294·31	9·110	30·95

The orthobaric densities of nitrogen dioxide are shown in Fig. 3 and lead to a critical density of 0·570 g. c.c.$^{-1}$ at a temperature of 158·20°.[17] More recently[13] the critical temperature has been given as 158·20°, the critical pressure as 99·96 atm., and the critical volume as 165·3 c.c. mol^{-1}.

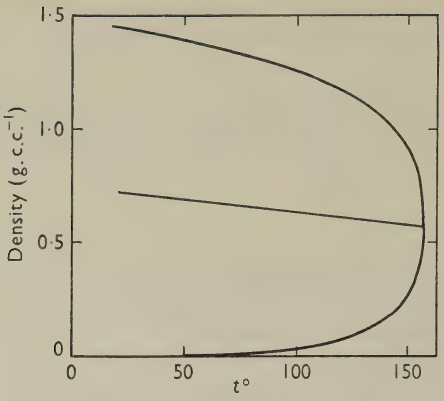


FIG. 3.—The orthobaric densities of nitrogen dioxide

The compressibility of nitrogen dioxide at 0° has been reported to be 14·7 × 10^{-6} per cm. of mercury. This leads to a value of 0·00112 for the coefficient A.[18] The volumetric behaviour under pressure of nitrogen dioxide above room temperature has been studied and is likely to be of technical importance.[13, 14]

The viscosity of liquid nitrogen dioxide has recently been measured with the results shown in Fig. 4.[19] Some results at lower temperatures are given by Bourjol[20] but in this case the nitrogen dioxide contained impurities.

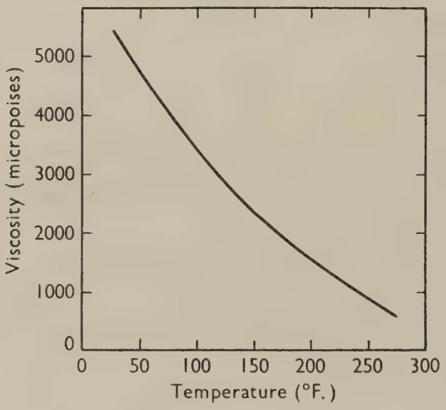


FIG. 4.—Viscosity of nitrogen dioxide in the liquid phase

The thermal conductivity of gaseous nitrogen dioxide has been examined under the influence of a magnetic field.[21]

Electrical Conductivity, Dipole Moment and Magnetic Susceptibility

The electrical conductivity of nitrogen dioxide has been measured in the liquid phase[22, 23] and the most recent and extensive results fit the equation[24]

$$\log \kappa = -1267/T - 8{\cdot}260$$

over the temperature range 21 to −25°, where κ is in int. ohm^{-1} cm.^{-1}. The extrapolated value at 25° is 3·1 × 10^{-13}. Measurements were also made on the solid, but these are less reliable since the material was polycrystalline.

Measurements of the electrical conductivity of nitrogen dioxide in nitromethane indicate that in this solvent nitrogen dioxide behaves as a very weak electrolyte.[25]

The results of measurements of the magnetic susceptibility of nitrogen dioxide agree within the experimental error with the values calculated by Van Vleck. The mole susceptibility of nitrogen dioxide is given by the expression: $1380(293/T) \times 10^{-6}$, where T is the absolute temperature.[26] The magnetic susceptibility of dinitrogen tetroxide, as measured by Soné,[27, 28] has the value $-0{\cdot}28 \times 10^{-6}$ (per unit mass). More recently the magnetic susceptibility of the equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide in the liquid phase has been studied over a range of temperatures to enable the equilibrium constant to be determined.[29] The liquid is diamagnetic and the susceptibilities are tabulated in Table V.

Table V.—Magnetic Susceptibility of Mixtures of Nitrogen Dioxide and Dinitrogen Tetroxide at Various Temperatures (per unit mass)

$t°$	susceptibility $\times 10^7$
30·6	−2·40
22·1	−2·50
15·0	−2·57
8·3	−2·67
−0·1	−2·72

The electric moments of nitrogen dioxide and dinitrogen tetroxide have been studied with some rather unusual results. Zahn[30] concluded that the dipole moment of nitrogen dioxide is 0·39 debye, while that of dinitrogen tetroxide is 0·55 debye. This finding was criticised since it had been shown that the molecular polarization of dinitrogen tetroxide does not change appreciably with temperature, which would suggest a zero dipole.[31] It was further reported that the measurements of the dielectric constant of mixtures of nitrogen dioxide and dinitrogen tetroxide can be interpreted in terms of a zero dipole moment for the dimer.[35] The experimental observations were not greatly different from those of Zahn. A later paper, however, gave results in agreement with those of Zahn.[32] Precision measurements of the dielectric constant of the gases as a function of temperature gave a result of 0·37 debye for dinitrogen tetroxide and of 0·29 debye for nitrogen dioxide. The result for dinitrogen tetroxide is taken to exclude a symmetrical structure for the molecule.

It appears that these results conflict only in the deductions drawn from them and it is probable that the correct interpretation is in terms of a zero dipole moment for dinitrogen tetroxide and a variable dipole moment for nitrogen dioxide.[80] The results for nitrogen dioxide with these assumptions are shown in Table VI.

Table VI.—Electric Moment of Nitrogen Dioxide as a Function of Temperature

$T°$K.	Electric moment (debye)
298·1	0·58
343·1	0·41
398·1	0·30

The dielectric constant of the liquid has recently been reported as 2·42 at 18°.[33] The molar polarization is found to be 26·5 c.c. and the molar refraction 15·2 c.c. The difference between these two quantities can in part be attributed to the presence of an ion pair $NO^+NO_3^-$. The molar polarization of the gas is 16·87 c.c.[31]

Structures of Nitrogen Dioxide and Dinitrogen Tetroxide

The structures of nitrogen dioxide and dinitrogen tetroxide are of considerable interest and will be considered separately.

The stereochemistry of nitrogen dioxide has been discussed in terms of the normal configuration of electrons in molecules.[36–38] Data for the refraction and dielectric properties of nitrogen dioxide are taken to indicate that the molecule is not linear[39] and the structure has been considered from the point of view of the Lewis octet theory.[40] The vibrational frequencies and form of the molecule have been quite extensively examined,[41–46] although much of this work is open to criticism.[47] Two of the three fundamental frequencies of nitrogen dioxide have been observed only recently.[48] The most recent determinations of the configuration of nitrogen dioxide from infra-red data[49, 50] yield a value of 134° 4′ for the angle ONO, with a nitrogen to oxygen distance of 1·188 A.

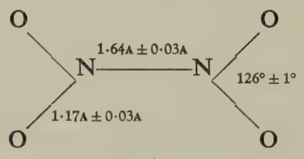
These values are confirmed by electron diffraction data[47, 51, 52] from which the latest workers find a value of 1·20 A. for the internuclear distance with an angle of 132°.[47]

The microwave spectrum of nitrogen dioxide has been studied,[53] and is being re-investigated.[54] A comparison of light diffraction patterns of models with electron diffraction patterns of the molecule yielded values for nitrogen dioxide close to those given above.[55]

The structure of dinitrogen tetroxide at temperatures below the melting point has unambiguously been shown to contain an N–N bond and to be symmetrical and planar. The evidence from its chemical behaviour at higher temperatures, however, points to a contribution by other structures, some of which are not insignificant in concentration.

X-Ray powder photographs of solid nitrogen dioxide were originally interpreted in terms of the monomer,[56, 57] but this work has been criticised and the results have been re-interpreted in terms of dimeric molecules with a space group for the crystal of either I_{23}, Im_{3} or $I_{43}m$.[58] The structure has been further discussed.[59, 60]

Broadley and Robertson[61] consider that the evidence of Vegard[56, 57] on powder specimens is inconclusive and have studied single crystals of dinitrogen tetroxide. The apparently cubic unit cell contains six molecules of dinitrogen tetroxide, the molecules being planar and having the dimensions indicated:



The density calculated from the *X*-ray work is 1·95 at −40°,[61] which agrees with the measured value. The density of dinitrogen tetroxide at −195°[62, 63] was found to be 1·979 g. c.c.$^{-1}$. The density of the liquid has also been measured,[64, 10] and some of the more recent results are shown in Table VII, although it should be noted that the purity of the material is in some doubt.[20]

Table VII.—Density of Liquid Dinitrogen Tetroxide

t°	Density (g. c.c.$^{-1}$)
15	1·453
10	1·460
5	1·462
0	1·469
−10	1·490

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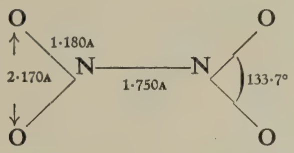
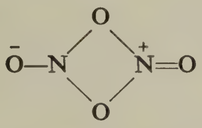
There have been a number of papers on the infra-red spectrum of dinitrogen tetroxide, the most important probably being that by Sutherland.[65] The most recent papers agree that the molecule is planar in the solid, and that the data can be interpreted in terms of the *X*-ray model.[66] It has indeed been stated that the molecule is planar in the gas, the liquid and the solid.[67]

The results of electron diffraction measurements on the gas at −20° (containing less than 25% of the monomer) show the molecule to have the following configuration[67]:

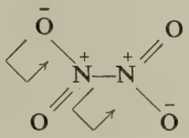


A theoretical study of the dinitrogen tetroxide molecule has also been made.[68, 73, 74]

The chemical reactions of dinitrogen tetroxide were considered originally only in terms of O_2N—NO_2, O_2N—ONO and ONO—ONO.[69,70] However in 1944 Longuet-Higgins[71] introduced an alternative structure:



The symmetrical structure for dinitrogen tetroxide, involving an N–N bond, violates Pauling's adjacent charge rule, whereas the symmetrical molecule shown above does not. Longuet-Higgins further suggested that the above formulation gives as good a fit for the Raman spectrum as the alternative symmetrical structure with an N–N bond. Ingold and Ingold considered the four possible formulations for the dinitrogen tetroxide molecule and concluded that the structure given below represents the best compromise between the physical and chemical evidence.[72]



Dinitrogen tetroxide has been considered as nitrosonium nitrate,[79] or nitrosyl nitrate,[75] and it has been shown that $Me_4N^{15}NO_3$ undergoes a quantitative exchange of the nitrate ion with liquid dinitrogen tetroxide.[76] It is preferable, however, to think in terms of a polarized ON—NO_3 in liquid dinitrogen tetroxide, rather than of the presence of ions.[77] The existence of nitrate ions in the liquid has been discussed,[78] and a mechanism for the dissociation[80] of dinitrogen tetroxide heterolytically to yield NO_2^+ and NO_2^-, followed by oxidative transfer of an oxygen atom to form NO^+ and NO_3^-, has been postulated.

A recent study of the reaction between dinitrogen tetroxide and iodide ion is held to show that a proportion of the ring form suggested by Longuet-Higgins must be present in the reaction mixture.[81] Similarly the nitration and nitrosation of amines and alcohols have been interpreted in terms of an equilibrium between ONO—NO_2 and O_2N—NO_2,[82] the latter being the predominant species.

Absorption Spectra

The absorption spectrum of gaseous nitrogen dioxide has been studied. Some results in the visible range are summarized in Fig. 5.[83] The absorption spectra of both dinitrogen tetroxide and nitrogen dioxide have been studied in the range 2400 to 5000 A.[84]

The fluorescence excited in nitrogen dioxide by ultra-violet light, and the quenching of this fluorescence by the addition of foreign gases, have been examined.[85–87]

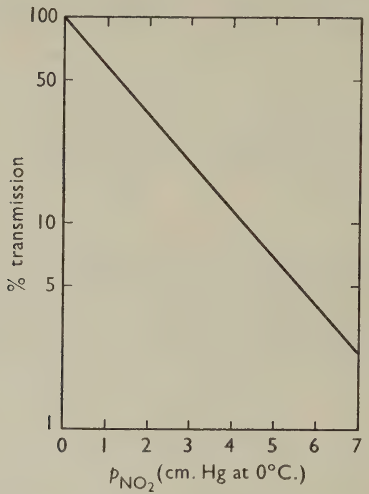


FIG. 5.—Absorption of light by nitrogen dioxide at wave-length 4850A

Miscellaneous Properties

The ionization potential of nitrogen dioxide to yield NO_2^+ has been measured approximately and given as 11ev.[88] A spectroscopic determination gives the rather higher result of 12·3ev.[89]

The range of α-particles in nitrogen dioxide,[90, 91] the impact of slow electrons[92] and the ionization method for measuring neutron energy[93] have been examined. Ionization produced in the decomposition of nitrogen dioxide has also been studied,[94] as has the possible formation of dimers under the effect of electric fields[95] and the behaviour of nitrogen dioxide in an electric discharge.[96, 97]

Equilibrium constants for isotopic exchange reactions involving ^{15}N in nitrogen dioxide have been calculated,[98] and measured[99] for the reaction:

$$^{14}NO + {}^{15}NO_2 \rightleftharpoons {}^{15}NO + {}^{14}NO_2$$

The equilibrium constant for this reaction is found to be 0·96 at 298·1°K.

Thermal diffusion in mixtures of nitrogen and hydrogen containing nitrogen dioxide has been investigated[100] and the Joule effect has been studied.[101] The life time of excited nitrogen dioxide molecules was found to be very long.[102]

Adsorption of nitrogen dioxide[103–106] has been studied and in view of its industrial importance has been mentioned earlier (p. 166). Work has also been reported on the magnetic properties of nitrogen dioxide adsorbed in various concentrations.[107, 108] For example, taking the magnetic susceptibility of nitrogen dioxide to be 39×10^{-6} and of dinitrogen tetroxide to be $-0{\cdot}28 \times 10^{-6}$, it was calculated that at a concentration of 0·02 g. of nitrogen dioxide per g. of silica gel the degree of dissociation of the tetroxide is 0·7% Adsorption by rutile[108–111] gives results in many ways similar to those obtained with silica gel, except that with rutile there is the added complication of chemisorption, resulting in the formation of nitric oxide. Sorption on stainless steel has also been examined.[112, 113]

Little is known of the solubility of nitrogen dioxide in organic solvents, and in the case of aqueous solutions reaction of course occurs. At room temperature 5 c.c. of nitrogen dioxide are reported to dissolve in 1 c.c. of sulphuric acid containing approximately 8% of HNO_3.[114] Adsorption by crystalline sodium chloride and its aqueous solution has been studied.[115] The vapour density of nitrogen dioxide over carbon tetrachloride solutions of this solute has been measured.[116] Phase diagrams of nitrogen dioxide with bromoform, carbon tetrachloride, bromobenzene, chloroform, chloropicrin, methyl iodide, picric acid, trinitrotoluene,[117] camphor,[117, 118] bromine,[119] sulphur dioxide,[120] nitric acid,[121] water,[122] dinitrogen pentoxide,[123], nitromethane,[25] diethylnitrosamine[124] and nitrosyl chloride[125] have been reported. The calculation of partial pressures of the components of a binary solution from observed total vapour pressure has been discussed for the system dinitrogen tetroxide and chloroform.[126]

The ionization of dinitrogen tetroxide in nitric acid has been studied.[127]

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THE REACTION $2NO_2 \rightleftharpoons N_2O_4$

The Rate of Decomposition of Dinitrogen Tetroxide

The velocity of sound in nitrogen dioxide–dinitrogen tetroxide mixtures may be used to determine the rate of dissociation of the tetroxide. This rate has been extensively studied,[1–5] but the exact interpretation of the data and the nature of the dispersion effects do not seem to be fully understood.[6, 7] Even later workers[8–12] do not appear to be able to agree on the interpretation of the results.

More recently it has been suggested that interpretation of acoustic measurements is uncertain owing to the slight effect observed and the uncertainty of the contribution of vibrational heat capacity lag and other factors.[14] The rate of dissociation, measured by a photoelectric study of nitrogen dioxide under the impact of shock waves,[14, 15] indicates that the lower limit of the first order rate constant for the dissociation of dinitrogen tetroxide at 25° is 1×10^6 sec.$^{-1}$, or

$$k = 10^{16} \exp(-13{,}000/RT)$$

The rate of reaction has also been examined by allowing an equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide to flow through a perforated diaphragm under a pressure drop and studying the temperature of the gas before and after expansion.[13] The rate constant for the decomposition of dinitrogen tetroxide was thus found to be between 2×10^4 and 8×10^4 sec.$^{-1}$ at 25°.

The Equilibrium $2NO_2 \rightleftharpoons N_2O_4$

This equilibrium is classically famous and has probably been studied by more investigators than has any other equilibrium. In view of the difference in the number of molecules on the two sides of the equation, the effect of pressure is of interest. The fact that nitrogen dioxide is coloured while dinitrogen tetroxide is colourless means that the effect of temperature on the equilibrium may be readily demonstrated. Nearly all determinations of the equilibrium constant have been made in the gaseous phase.

The investigations range from simple observations that on plunging a tube containing nitrogen dioxide into cold water the contents become almost colourless and that by subsequently heating the tube a dark brown colour is seen,[16] to the classical researches of Bodenstein.[17] The earlier work on this equilibrium[17–19] has been admirably summarized and collated by Giauque and Kemp.[20] By correcting for gas imperfections they find that near the boiling point the behaviour may be represented by an equation of the type:

$$p_1 v = RT(1 + \lambda p)$$

where p is the total gas pressure, and λ for NO_2 is taken as that calculated for CO_2 using Berthelot's equation of state. The corresponding value of λ for N_2O_4 is arbitrarily put at $-0{\cdot}01$, that for NO_2 being $-0{\cdot}005$. It can be shown that λ is approximately proportional to T^{-3} so that $\lambda_{N_2O_4}=2\lambda_{NO_2}=\beta=-0{\cdot}01(294/T)^3$. In this case K may be written:

$$K=\frac{4p(\alpha'+\beta p^2)}{1-(\alpha'+\beta p^2)}$$

The following values of α' at various temperatures are quoted:

T°K.	α'
281·82	0·1593
294·20	0·1773
320·29	0·4192
356·03	0·7559

Later results for the equilibrium have in general been in good agreement with earlier work.[21–23] The equilibrium in a solution in carbon tetrachloride has also been studied.[24]

Measurements of the equilibrium constant in pure liquid nitrogen dioxide are rare, but two recent determinations using spectrophotometry and magnetic susceptibility are in good agreement.[25, 26]

The data concerning the effect of intensive drying on the vapour pressure, dissociation constant and other physical properties of nitrogen dioxide[27–32] are now considered to be valueless in view of the reported reaction of dinitrogen tetroxide with the desiccant.[33]

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REACTIONS OF THE MIXTURE: NITROGEN DIOXIDE AND DINITROGEN TETROXIDE

The Reaction between Nitrogen Dioxide and Hydrogen

The stoicheiometry of the reaction between nitrogen and hydrogen may be represented by the equation[1, 2, 3]:

$$NO_2 + H_2 \rightarrow NO + H_2O$$

The rate of the reaction is greater than the rate of the bimolecular decomposition of nitrogen dioxide, and the reaction is inhibited by nitric oxide owing to termination of chains. The following reaction scheme has been suggested:

$$\begin{aligned} &H_2 + NO_2 \rightarrow H + HNO_2 \\ &H + NO_2 \rightarrow NO + OH \\ &OH + H_2 \rightarrow H_2O + H \\ &OH + NO_2 + (M) \rightarrow HNO_3 + (M) \\ &OH + NO + (M) \rightarrow HNO_2 + (M) \end{aligned}$$

Addition of small quantities of nitrogen dioxide to a mixture of hydrogen and oxygen has a considerable effect on both the slow reaction and the explosion.[4–21] Low concentrations appreciably depress the ignition temperature (sometimes by several hundred degrees) and the upper and lower explosion limits may be affected. Some results for hydrogen and air mixtures are shown in Table VIII.[20]

Table VIII.—Upper and Lower Explosion Limits for Hydrogen and Air Mixtures in the Presence of Nitrogen Dioxide

% Nitrogen dioxide	Volume % of hydrogen upper limit	Volume % of hydrogen lower limit
0	74·6	4·19
0·26	73·7	4·15
0·52	72·9	4·10
0·92	71·7	4·18

Although the addition of nitrogen dioxide lowers the upper limit proportionally to the quantity added, the absence of characteristic emission shows that this is not due to the reaction:

$$NO + O \rightarrow NO_2 + h\nu$$

The formation of ammonia by the action of an electric discharge on a mixture of nitrogen dioxide and hydrogen has been discussed,[22] and the ortho-para hydrogen conversion under the influence of the paramagnetic nitrogen dioxide molecule has been examined.[23]

Reactions with Carbon Monoxide and Carbon Disulphide

It has been suggested[24] that the initial step in the reaction of nitrogen dioxide with carbon monoxide may be written:

$$CO + NO_2 \rightarrow CO.NO_2$$

This reaction has been examined[25, 26] and shown to yield initially nitric oxide and carbon dioxide. The reaction between carbon monoxide and oxygen is sensitized by nitrogen dioxide and it appears that nitrogen dioxide is responsible for the chain branching.[27–29]

The explosion limits of mixtures of carbon disulphide and nitrogen dioxide have been given as $CS_2:NO_2$ 1:5·55 and 1:0·40, on a mole basis.[30] The products of the reaction were complex.

Reactions with Oxygen, Ozone and Atomic Oxygen

It has been known for a considerable time that ozone and nitrogen dioxide react very rapidly to produce dinitrogen pentoxide.[31] It was[32] suggested that the reaction mechanism is:

$$NO_2+O_3 \rightarrow NO_3+O_2$$

$$NO_3+NO_2 \rightarrow N_2O_5$$

This mechanism is in agreement with that proposed more recently.[33] The rate of reaction has been measured[34] and the activation energy was found to be only 7 kcal. mole^{-1}.

The action of atomic oxygen on nitrogen dioxide is accompanied by a yellowish glow.[35–37] Although the formation of nitrogen trioxide by passing a mixture of nitrogen dioxide and oxygen over aluminium electrodes having a potential difference of 6·5kv. has been reported,[38] other experiments showed that no higher oxide of nitrogen was produced on passing a glow discharge through such mixtures.[39]

Reactions with Oxides, Hydroxides and Carbonates

Much work has been done on the action of nitrogen dioxide on metal oxides. Early workers found that calcium oxide when heated in an electric furnace and treated with nitrogen dioxide gives a mixture of nitrate and nitrite.[40] It was also noted that calcium nitrite is not oxidized by oxygen below 230°, but that with addition of nitrogen dioxide to the oxygen oxidation occurs. The lack of reaction between nitrogen dioxide and cuprous oxide was shown, although the oxide takes up at least 30% of its weight of nitrogen dioxide from the gaseous phase.[41,42] With lead dioxide, used for the sorption of oxides of nitrogen during micro-combustions, the following reaction is reported to occur[43]:

$$2NO_2+2PbO_2 \rightarrow Pb(NO_3)_2{,}PbO+\tfrac{1}{2}O_2$$

At most only a trace of nitrite was detected.

Higher oxides of the 'actinide' elements cannot in general be prepared by the action of oxygen on an oxide or the element. It has been found, however, that treatment of U_3O_8 with nitrogen dioxide at 250–350° gives a brick-red variety of UO_3.[44] Similarly dried hydroxides precipitated from solutions containing tetra-, penta- or hexa-valent neptunium all yield Np_3O_8. It was suggested that nitrogen dioxide is a more efficient oxidizing agent than oxygen in the temperature range 100–500° owing to the formation of atomic oxygen by dissociation. Plutonium, americium and protactinium do not form higher oxides by this reaction. The hydrates $UO_4{,}2H_2O$ and $UO_3{,}2H_2O$ were found to react with liquid nitrogen dioxide to yield a hydrated uranyl nitrate, containing nitrogen dioxide of crystallization.[45] With the anhydrous oxides the solvated anhydrous nitrates are formed.

The action of nitrogen dioxide on oxides has been discussed[46] and examined[47] recently. Liquid and gaseous nitrogen dioxide react with sodium peroxide, calcium oxide and zinc oxide below 140° to yield exclusively the nitrates; nitrites are not formed as intermediates. Similar reactions occur above 140°, but with some formation of nitrite; the amount of nitrite increases with temperature but decreases relatively with time of contact. These effects may be interpreted in terms of the reaction:

$$Na_2O_2+2NO \rightarrow 2NaNO_2$$

followed by:

$$NaNO_2+O \rightarrow NaNO_3$$

The atomic oxygen is supposed to be produced by the impact of nitrogen dioxide on the surface of the nitrite.

A more general approach to this problem indicated the not surprising fact that oxides prepared at a higher temperature are less reactive than those produced at lower temperatures.[48] Marked catalysis by water was also noted. The products are either the anhydrous nitrates or the solvated nitrates. Barium peroxide has been reported to yield only nitrate on treatment with nitrogen dioxide between 0° and 400°, the quantity of nitrate increasing with the time of contact.[49]

The supposed equilibrium between nitrogen dioxide, oxygen, cupric oxide and hydrated cupric nitrate has been examined,[50] as has the effect of nitrogen dioxide on manganese ores in the presence of water.[51]

The reaction of nitrogen dioxide with potassium hydroxide has been studied[52] and more recent work indicates that with anhydrous solid sodium hydroxide 94% is converted into nitrate, whilst only 2·5% of nitrite is found under the same conditions.[53] It appears that with carbonates the main product is again nitrate[53–55]; a selection of results is shown in Table IX.

Table IX.—The Action of Nitrogen Dioxide on Sodium Carbonate under Various Conditions

Time of contact	Temperature	% Nitrate	% Nitrite
19 hr.	250°	49	10
24	250°	64	12·3
19	600°	10·2	0·0
24	600°	14·6	0·0

These results are interepreted in terms of the reaction:

$$Na_2CO_3 + 2N_2O_4 \rightarrow 2NaNO_3 + CO_2 + N_2O_3$$

which is very sensitive to traces of moisture.

Reactions with Sulphur Dioxide and Sulphur Trioxide

Of numerous publications on the reaction between nitrogen dioxide and sulphur dioxide, most of the more recent are from Russia. It has been reported that by passing dry nitric oxide into liquid sulphur trioxide there occurs at 60° a reaction, from which a crystalline hygroscopic solid having the composition $(SO_3)_2NO$ may be isolated. The same compound may be produced from nitrogen dioxide and sulphur dioxide.[56] Subsequent work has verified the formula NS_2O_7, although it has been suggested that the initial reaction is:

$$\tfrac{3}{2}N_2O_4 + 2SO_2 \rightarrow S_2N_2O_9 + NO$$

the $S_2N_2O_9$ readily losing nitrogen dioxide to give S_2NO_7.[57] The compound $S_2N_2O_9$ behaved as an anhydride of nitrosyl bisulphate with water, alkali or sulphur dioxide. It has further been shown that the compound $2SO_3,N_2O_3$ is formed by the reaction of dinitrogen trioxide with sulphur dioxide or of nitric oxide with sulphur trioxide.[58] This compound has also been found in studies of the phase diagram for the system nitrogen dioxide and sulphur dioxide.[59] More recently it has been suggested that these reactions do not occur in the absence of water vapour,[60, 61] but since phosphoric oxide, used as the drying agent, reacts with nitrogen dioxide the results are suspect. The kinetics of these reactions have been studied.[62–65] The compound $N_2O_3,2SO_3$ or $N_2S_2O_9$ may be formulated as $(NO)_2S_2O_7$,[66] and the compounds $N_2O_5,3SO_3$ and $N_2O_4,3SO_3$ have been similarly formulated as $(NO_2)_2S_3O_{10}$ and $(NO)(NO_2)S_3O_{10}$.[67]

Refs. p. 265

Reactions with Halogens, Halides, Halites and Halates

Although nitrogen dioxide and chlorine react only slowly to form nitryl chloride,[155, 156] the corresponding reaction with fluorine is used as a means of preparing nitryl fluoride, NO_2F,[68] and the kinetics of this reaction have been studied.[69, 70]

Iodine pentafluoride reacts with nitrogen dioxide to yield IF_5,NO_2 which is an easily sublimed, thermally unstable, cream coloured solid.[71]

The reaction of nitrogen dioxide with potassium chloride containing 2% by weight of water is of value in the preparation of nitrosyl chloride. It was at one time of interest industrially for the production of potassium nitrate.[72] The function of water in catalysing this reaction has been discussed[73] and the free energy change in the reaction has been given.[74] The reaction has been further studied[75, 76, 85] and the formation of alkali nitrate crystals on alkali halides has been examined.[77, 78]

The interaction of nitrogen dioxide and iodide ions, already mentioned in connection with the preparation of nitric oxide (see p. 218), has been studied quite extensively by Dodé[79–82] and others.[83] The most recent workers have examined the effects of varying the iodide ion concentration, the total pressure and the temperature.[84] The two main reactions considered are:

$$N_2O_4 + 2I^- \rightarrow 2NO_2^- + I_2$$

$$N_2O_4 + I^- \rightarrow NO_3^- + \tfrac{1}{2}I_2 + NO$$

Several other reactions were also considered; among them may be mentioned:

$$2NO + N_2O_4 \rightarrow 2N_2O_3$$

and

$$2NO_2^- + \tfrac{1}{2}I_2 \rightarrow NO_3^- + NO + I^-$$

The mechanism of the dissociation of dinitrogen tetroxide has been discussed (see p. 257).

The reaction of nitrogen dioxide with cupric chloride has been shown to result in partial conversion to the nitrate.[85]

Dinitrogen tetroxide reacts with boron trifluoride to yield a polar compound formulated as $F_3B,NO_2^-NO_2^+$.[86] This compound may be of value in carrying out organic reactions. It appears that nitrogen dioxide has no effect on silicon tetrafluoride,[87] although with antimony pentafluoride a product having the formula SbF_5,NO_2 is formed.[88]

Stannic chloride is reported to form the compound $SnCl_4,5/2NO_2$, while titanium tetrachloride reacts to form the tetranitrate as well as some $TiCl_4,2NOCl$.[89] With nitrogen trichloride a variety of products is obtained,[90] while tellurium dichloride yields the dioxide and nitrosyl chloride.[91]

After six hours a mixture of sulphuryl chloride and nitrogen dioxide[92] at 180° yields the white crystalline solid $N_2S_2O_9$, discussed above.

The reaction of nitrogen dioxide with hydrogen chloride is thought to be represented by the equation[93]:

$$NO_2 + 2HCl \rightarrow NOCl + H_2O + \tfrac{1}{2}Cl_2$$

With phosphorus tribromide and oxygen, nitrogen dioxide acts as a catalyst for the production of the oxybromide.[94]

By passing a mixture of nitrogen dioxide and air through sodium chlorite solution it is possible to produce chlorine dioxide,[95, 96] the reaction being:

$$NO_2 + NaClO_2 \rightarrow ClO_2 + NaNO_2$$

Similarly chlorine dioxide may be produced by the action of nitrogen dioxide on chloric acid in aqueous nitric acid[97] or on a moist chlorate.[98–100]

Reactions with Nitrites, Hyponitrites, Nitrates and Amides

It has been suggested[101] that the reaction:

$$NaNO_2 + NO_2 \rightarrow NaNO_3 + NO$$

is reversible at approximately 400°. It appears that certain nitrites are not affected by liquid dinitrogen tetroxide,[47] and that the oxidation to nitrate which occurs at high temperature is in fact due to atomic oxygen produced by collision of the nitrogen dioxide molecules with the surface of the nitrite, yielding nitric oxide at the same time. Any nitrite which decomposes may appear to react, owing to the reaction of the products of the decomposition.[102]

The induced decomposition of hyponitrites has been reported to take place at 0° in the presence of nitrogen dioxide.[102] The reactions that occur are those found in the thermal decomposition of hyponitrites:

$$M_2N_2O_2 \rightarrow M_2O + N_2O$$
$$3M_2N_2O_2 \rightarrow 2M_2O + 2MNO_2 + 2N_2$$

These results appear to be quite different from those of Addison, Gamlen and Thompson[103] who find that unlike nitrite and nitrate, hyponitrite and oxyhyponitrite ($Na_2N_2O_3$) are immediately oxidized by liquid nitrogen dioxide.

The explosive decomposition of triethylammonium nitrate and nitrogen dioxide mixtures has been mentioned[104] and the reaction of sodamide with nitrogen dioxide in carbon tetrachloride solution has been shown to result in the production of the amidonitrate.[105]

The Action of Nitrogen Dioxide on Metals

Nitrogen dioxide readily attacks many metals and several papers describing such reactions are of a technical nature. Earlier work indicated that nitrogen dioxide attacks iron and copper,[106, 107] and it was later suggested[108] that in the case of copper the product is the oxide, Cu_2O. With mercury the products of reaction were thought to be mercurous nitrite and mercuric nitrite.[154] Recently[109] the reaction has been shown to be represented by the equation:

$$4Hg + 6NO_2 \rightarrow Hg_2(NO_3)_2 + Hg_2(NO_2)_2 + 2NO$$

The reaction of selenium with gaseous nitrogen dioxide produces selenium dioxide.[110] The interaction of nitrogen dioxide with atomic sodium results in a powerful chemiluminescence[111] which has been attributed to the following scheme[112]:

$$\begin{aligned}&Na + NO_2 \rightarrow NaO + NO\\&NaO + Na_2 \rightarrow Na_2O^* + Na\\&Na_2O^* + Na \rightarrow Na_2O + Na^*\\&Na^* \rightarrow Na + h\nu\end{aligned}$$

Frequently the reaction of nitrogen dioxide in the liquid phase with a metal results in the formation of an adherent film which slows down any subsequent reaction. This is apparently not so with zinc and hence the reaction with this element has been thoroughly examined. The alkali metals react rapidly and controllably with liquid dinitrogen tetroxide to yield the corresponding nitrates but no nitrite.[46] Zinc reacts readily with nitrogen dioxide to give a white crystalline solid, insoluble in nitrogen dioxide, and having the formula $Zn(NO_3)_2,2N_2O_4$.[113] At 100° the pure anhydrous nitrate is formed. The kinetics of this reaction have been examined[114] as has the effect of the addition of dinitrogen trioxide or nitrosyl chloride. In the former case no additional compounds are formed, although the rate of reaction is increased.[115] With nitrosyl chloride, depending on the conditions of reaction, it is possible to obtain the chloride or the nitrate, sometimes solvated.[116]

Solutions of diethylnitrosamine in dinitrogen tetroxide behave in a manner that may be interpreted in terms of the following equilibria[117]:

$$N_2O_4 + 2Et_2NNO \rightleftharpoons N_2O_4,2Et_2NNO \rightleftharpoons (Et_2NNO)_2NO^+ + NO_3^-$$

Zinc reacts with these solutions to yield a red liquid, immiscible with nitrogen dioxide,[118] which is the same as the solution obtained by dissolving $Zn(NO_3)_2 2N_2O_4$

in diethylnitrosamine. It was further shown that the following equilibrium exists in solution:

$$Zn(NO_3)_2+2N_2O_4+4Et_2NNO \rightleftharpoons [(Et_2NNO)_2NO^+]_2[Zn(NO_3)_4^{--}]$$

These reactions are similar to those found with zinc hydroxide and aqueous solutions of alkali hydroxides. Ethylammonium tetranitratozincate has similarly been prepared[119] and the equilibrium between alkylammonium and nitrosonium tetranitratozincates has been studied.[120]

It has been observed that the rate of reaction of nitrogen dioxide with metals may be considerably enhanced when the nitrogen dioxide is dissolved in an organic solvent which may act as a donor. Under these conditions the following equilibria apply[121]:

$$[(\text{donor})_nNO^+]NO_3^- \rightleftharpoons n(\text{donor})+N_2O_4 \rightleftharpoons (\text{donor})_nN_2O_4$$

The reaction with copper is of particular interest.[122] Copper reacts rapidly with a mixture of nitrogen dioxide and ethyl acetate, a crystalline product having the formula $Cu(NO_3)_2,N_2O_4$ being obtained from the solution. This compound loses nitrogen dioxide at 85° to leave the pure nitrate which can be sublimed unchanged in a vacuum. The properties of the nitrate indicate considerable covalent character.

The extent and prevention of corrosion of steel plant caused by contamination of circulating water with nitrogen dioxide have been discussed.[123]

Explosions with Nitrogen Dioxide

Several gas phase reactions involving nitrogen dioxide show well defined regions where explosion occurs. In a number of cases organic reagents have been found to react explosively with this compound. In 1955 a research worker was killed while studying the preparation of alkyl nitrates from nitrogen dioxide and alcohols.[124] There was an industrial explosion at Zschornewitz, but the most serious one occurred at the works at Bodio in Switzerland[125–129] where a large quantity of nitrogen dioxide became mixed with petroleum. An attempt was made to distil the mixture and in the resulting explosion 17 men were killed and the works devastated. At Zschornewitz nitrogen dioxide and toluene were accidentally mixed. It appears that the initial detonation may have been due to the presence of impurities, notably unsaturated compounds. Nitrogen dioxide and nitrobenzene mixtures have been studied as possible military explosives.[130]

Reactions with Organo-metallic Compounds, Carbonyls and other Organic Compounds

Phenyl mercuric chloride and mercury diphenyl react with nitrogen dioxide to yield mainly benzyl nitrite and benzyl nitrate.[131] With mercury diethyl and dibutyl the products of reaction are (alkyl)$HgNO_3$ where the reaction is carried out near $-10°$. The etherate of aluminium triethyl and nitrogen dioxide give a product which when hydrolysed yields diethylhydroxylamine.[132] According to Frazer and Trout,[133] nitrogen dioxide reacts with nickel carbonyl at temperatures above $-78°$, forming nickel nitrite and nickel nitrate. Nitrogen dioxide has been suggested as a reagent for the deleading of petrol,[134] and its reaction with organometallic compounds has been discussed.[135]

Although the organic reactions of nitrogen dioxide have little place in this account, the formation of addition compounds is of some interest. For example, addition compounds with ether, tetrahydrofuran, tetrahydropyran and dioxan have been reported.[136] No ternary compound is formed in the system dioxan, tetrahydropyran and nitrogen dioxide, which is held to indicate that the compound with dioxan is bicyclic.[137] Considering dinitrogen tetroxide as nitrosonium nitrate, the nitrosonium ion can accept two electron pairs. It is therefore possible to write the following scheme[138] where L is an electron donor ligand:

$$\begin{array}{ccc} N_2O_4 & \rightleftharpoons & NO^+ + NO_3^- \\ \downarrow 2L & & \downarrow 2L \\ 2L.N_2O_4 & \rightleftharpoons & 2L.NO^+ + NO_3^- \end{array}$$

It has been assumed that where onium electron donors are present (for example carboxylic acids) the complexes are 1:2, but in the case of π electron donors the complexes are 1:1.[139] Double melting of compounds of dinitrogen tetroxide with organic donors has been reported.[140]

Miscellaneous Reactions

Solutions of sodium stannite reduce nitrogen dioxide to ammonia,[141] while gaseous nitrogen dioxide reacts with ammonia to give a variety of products.[142]

The influence of nitrogen dioxide on the glow of phosphorus has been studied.[143] It has been found that calcium phosphate does not react with nitrogen dioxide if both the reactants are quite dry,[144] but in the presence of water reaction occurs to yield the nitrate. The reaction between nitrogen dioxide and phosphoric oxide yields the product $P_2O_5,2NO$,[145] with the simultaneous evolution of oxygen. When nitrogen dioxide has been dried by prolonged contact with phosphoric oxide, the product is likely to be contaminated with oxygen.

Tetrasulphurtetranitride, $(SN)_4$, and nitrogen dioxide yield colourless crystalline $N_2S_2O_9$.[146] It has been reported that when a glow discharge is passed through a mixture of nitrogen dioxide and bromine oxide at liquid air temperatures, the product is a white solid, $BrO_2,3NO_2$.[147]

The velocity constant for the oxidation of ferrous ion by nitrogen dioxide has been determined.[148]

The preparation of acetic anhydride by the action of nitrogen dioxide on sodium acetate has been studied[149, 150] and nitrogen dioxide has been investigated as a constituent of rocket fuels.[151, 152]

The ion $N_2O_3^+$ has been obtained by the reaction between nitronium ions and nitric oxide and between nitrosonium ions and nitrogen dioxide.[153]

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SECTION XXVIII

DINITROGEN PENTOXIDE

BY I. R. BEATTIE

PREPARATION

Dinitrogen pentoxide may be produced in the arc process for the fixation of nitrogen and also when chlorine reacts with silver nitrate. The formation of dinitrogen pentoxide during the reaction between nitric oxide and oxygen,[1] and by the action of ozone[2] or atomic oxygen[3] on nitric oxide has been reported.

Electrolysis of a solution of dinitrogen tetroxide in nitric acid under suitable conditions has been shown to yield 80% oxidation of the tetroxide to pentoxide, with a current efficiency of 35%.[4] The reaction is:

$$2NO_3^- + N_2O_4 \rightarrow 2N_2O_5 + 2e$$

The main reactions used for the preparation of dinitrogen pentoxide are the dehydration of nitric acid with phosphoric oxide and the oxidation of nitrogen dioxide with ozone. The latter reaction, already mentioned (p. 260), has been extensively studied.[5–9] In a recent paper describing the preparation of the pentoxide by this method[10] it is pointed out that because of the difficulty of drying nitrogen dioxide it is preferable to prepare dry nitric oxide and then to oxidize this to the dioxide using previously dried oxygen. The mixing tube must be sufficiently long to ensure nearly complete reaction, the residual nitric oxide at the outflow end being only 0·1%. Pre-dried oxygen is ozonized and added to the nitrogen dioxide stream so that there is an excess over the theoretical requirement. It was found necessary to allow the ozone stream to enter the nitrogen dioxide from four distinct branches, rather from one single connection; in this way nearly ideal utilization of the ozone occurred. The resultant dinitrogen pentoxide is collected on the walls of a glass spiral immersed in solid carbon dioxide. If the system is initially flushed out without cooling this trap and the level of the coolant is then slowly raised, a uniform coating is obtained on the spiral and so risk of blockage is reduced. The dinitrogen pentoxide thus obtained was found to contain less than 0·1% of nitric acid.

By adding nitric acid dropwise to a large excess of phosphoric oxide in a water-cooled flask it is possible to obtain dinitrogen pentoxide on gentle local heating.[11] More recently this preparation has been described in some detail.[12] The reaction is:

$$2HONO_2 + P_2O_5 \rightarrow N_2O_5 + 2(HPO_3)$$

where (HPO_3) is not taken to be a definite compound. Oxygen is initially passed through sulphuric acid contained in bottle *A* (see Fig. 1), and passes through glass wool in *B* into the ozonizer *C*. Ground glass joints are of course advisable, though cork stoppers coated with paraffin wax may be used. The receiver *E* is initially disconnected. The reaction flask *D* contains about 100 g. of colourless nitric acid, and oxygen is bubbled through this for about 10 minutes. The acid in *D* is then completely frozen, leaving no residue of liquid, while oxygen is still passing (presumably with the inlet tube for oxygen above the level of the solid); then the receiver *E* is connected, together with *F* and *G*. When oxygen has passed for several minutes to eliminate any traces of moisture, the receiver *E* is surrounded by a solid carbon dioxide cooling mixture. About 125 g. of phosphoric oxide is rapidly spread on the surface of the solid nitric acid, the cooling bath is removed from *D* and replaced by a water bath at room temperature and the ozonizer switched on. After the initial vigorous reaction has subsided the reaction mixture is agitated, causing a fresh stream of gas to be evolved and finally the water bath is heated to about 40° for a few hours to complete the reaction. After removing the water bath, ozonized oxygen should be allowed to flow for at least one hour longer to convert the nitrogen dioxide to pentoxide. A purer product is obtained if there is a reasonable span of time between the two sequences of reaction and if warming is gradual and possibly intermittent. The yield of dinitrogen pentoxide from this preparation should be of the order of 42 g. of pure product.

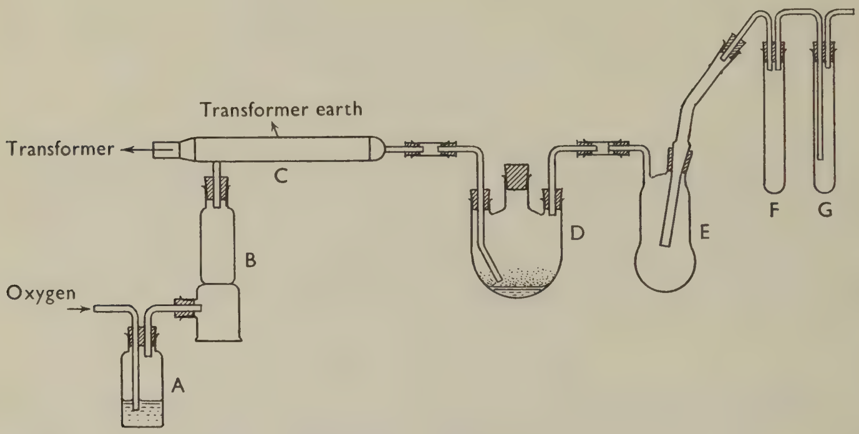

FIG. 1.—Preparation of dinitrogen pentoxide

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PHYSICAL PROPERTIES OF DINITROGEN PENTOXIDE

Thermodynamic Properties

Surprisingly little is known of the physical properties of dinitrogen pentoxide, probably owing to the fact that it is not thermally stable. The heat capacity between 90°K. and 250°K. has been measured with the results shown in Table I.

Table I.—The Heat Capacity and Entropy of Dinitrogen Pentoxide

T°K.	C_p (g.-cal. mole^{-1})	S (g.-cal. mole^{-1})
100	15·35	12·39
150	21·65	19·85
200	26·45	26·78
250	30·10	33·09

The heat of formation of crystalline dinitrogen pentoxide from its elements was found by Ogg[2] to be 9·6 kcal. mole^{-1}, while for the formation of the gas the value $3{\cdot}06 \pm 0{\cdot}20$ kcal. mole^{-1} has more recently been given.[3]

The vapour pressure of dinitrogen pentoxide has been measured up to 1 atm.[4] and it was found that the experimental results could be interpreted in terms of the empirical equation:

$$\log p\,(\text{mm.}) = 1244/T + 34{\cdot}1\,(\log T) - 85{\cdot}929$$

The heat of sublimation, calculated from the vapour pressure data by means of the Clapeyron–Clausius equation, has the values shown in Table II.

Table II.—Heat of Sublimation of Dinitrogen Pentoxide at Various Temperatures (calculated from vapour pressure data)

T°K.	Heat of sublimation (kcal. mole^{-1})
263	12·360
273	12·760
283	13·360
298	14·040
305·5 (extrapolated)	14·970

The compound sublimes at 32·5°, and does not melt below this temperature.

The values selected by the National Bureau of Standards differ somewhat from the data given above and are summarized in Table III.[5]

Table III.—Selected Values of Thermodynamic Functions for Dinitrogen Pentoxide

ΔH_f at 298·16°K. (for the gas)	3·6 kcal. mole^{-1}

Sublimation (crystal to gas):

t°	T°K.	p (mm.)	ΔH (kcal. mole^{-1})	ΔS (g.-cal. mole^{-1})
32·4	305·6	760	13·6	44·5

Structure

The structure of dinitrogen pentoxide has been discussed,[6, 7] and Pauling has postulated certain resonance structures.[8] The existence of nitronium ions in dinitrogen pentoxide has been suggested in view of the reaction between sodium and liquid dinitrogen pentoxide to yield nitrogen dioxide and sodium nitrate.[9] This could of course result from polarized $\overset{\delta+}{NO_2}\text{—}\overset{\delta-}{NO_3}$.

The crystal structure of dinitrogen pentoxide has been completely resolved and the solid should really be referred to as nitronium nitrate since it is fully ionic.[10, 11] The space group is *C*6/*mmc*. The density calculated from the *X*-ray data is 2·14 g. c.c.$^{-1}$ at −60°, which may be compared with the measured densities of 2·05 g. c.c.$^{-1}$ at 15°[12] and 2·175 g. c.c.$^{-1}$ at −195°.[13, 14] The molecular volume of dinitrogen pentoxide has been discussed.[15, 16]

The Raman spectrum of solid dinitrogen pentoxide and of concentrated aqueous solutions differs from that of solutions in non-polar solvents. There are two intense bands, one at 1050 cm.$^{-1}$ and the other at 1400 cm.$^{-1}$, which are attributed respectively to nitrate and nitronium ions.[17] Recent infra-red data also support this formulation.[18] The infra-red spectrum of the gas has been studied.[19]

The electron diffraction pattern of the gas has been shown to be consistent with an oxygen bridge between two NO_2 groups.[20]

Miscellaneous Properties

The viscosity of gaseous dinitrogen pentoxide has been measured relative to that of air and oxygen at 4°,[21] and the molecular diameter has been calculated.[21, 22]

Dinitrogen pentoxide is diamagnetic, the susceptibility being $-0{\cdot}03 \times 10^{-6}$ (per unit mass).[23]

Solutions of dinitrogen pentoxide in nitric acid have been examined by cryoscopic techniques,[24] and the system dinitrogen tetroxide–dinitrogen pentoxide shows one simple eutectic.[25]

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DECOMPOSITION OF DINITROGEN PENTOXIDE

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

This is classically important as a reaction which appears to remain 'unimolecular' over a wide range of experimental conditions. In 1925 Hunt and Daniels[1] wrote 'At present this reaction appears to stand as the sole survivor of the group of truly unimolecular reactions.' In the years immediately following (1926–1930) no less than twenty-five publications appeared dealing with the decomposition of dinitrogen pentoxide.

Earlier studies of the subject showed the reaction to follow a unimolecular rate law between 0° and 65°, with an energy of activation equal to 24·7 kcal. mol.$^{-1}$ and independent of the temperature. Although pure dinitrogen pentoxide had been used in most of the experiments, the operation of sealing off the apparatus before a run usually resulted in the formation of nitrogen dioxide owing to the thermal instability of the pentoxide. In a series of experiments where this nitrogen dioxide was oxidized by ozone,[3] it was apparently shown that the reaction was autocatalytic. There has been no subsequent support for this work and, in view of the clear absence of any such effect in any later publications where the work was repeated, this isolated result may now be rejected.[4–6]

It seems that the effect of accidental impurities and heterogeneous catalysts in this decomposition is small. For example, Hirst and Rideal[7] found that a platinum wire and a glass surface were without action. In an extensive investigation of the effect of dusts generally it was noted in particular that phosphoric oxide did not exert any catalytic influence.[8] There is however an instance of the rather extraordinary decomposition of dinitrogen pentoxide on a platinum surface at 0° to yield nitrous oxide and oxygen.[9] Moreover it has been pointed out that at very low pressures a not inconsiderable portion of the dinitrogen pentoxide may be adsorbed on to the walls of the containing vessel.[10]

In view of the various theories current around 1925 it is not surprising that the decomposition at low pressures should have been closely examined. The results for the decomposition at very low pressures were initially discordant, Hirst and Rideal for example finding an increase in the velocity constant at pressures below 0·26 and 0·28 mm.,[7] while Hibben found a decrease at lower pressures.[11] Later work[12] generally showed agreement with that of Daniels and Johnston,[13] except at lower pressures where there is a definite falling off in the rate.[14–17] This has been discussed,[18] and it appears that the region below which the reaction is no longer of first order is limited by a pressure of about 0·05 mm. It has been reported that below 0·004 mm. the reaction is bimolecular.[17]

It has been supposed that below certain pressures the reaction does not go to completion and that undecomposed dinitrogen pentoxide can be shown to exist even though reaction has ceased.[19, 20] Again it seems that these results are suspect.

The early results on the decomposition of dinitrogen pentoxide were applied as a test of the radiation hypothesis of Trautz, Lewis and Perrin. Using the value found experimentally for the energy of activation, it was calculated that light of wavelength 1·16 μ should cause decomposition.[21] This was not verified by the experimental results. These results and the general theory of 'unimolecular' reactions have been much discussed.[22–34]

Work on the thermal decomposition of dinitrogen pentoxide has been recently extended to higher temperature ranges,[35] yielding results in excellent agreement with those obtained earlier and at lower temperatures. The decomposition has also been studied in a flow system.[36] However the main interest has been in the mechanism of the reaction and most of this can be said to have arisen from a suggestion by Ogg[37] that the decomposition should be considered in terms of the following scheme:

$$N_2O_5 \rightarrow NO_2 + NO_3$$
$$NO_2 + NO_3 \rightarrow N_2O_5$$
$$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$$
$$NO + N_2O_5 \rightarrow 3NO_2 \text{ (rapid)}$$

This scheme has been discussed in connection with the previously mentioned approach.[38] It was subsequently shown[39] that $^{13}NO_2$ undergoes rapid exchange with N_2O_5, the reaction being conducted in carbon tetrachloride for convenience in dealing with the short half-life of ^{13}N. The equilibrium:

$$^{14}N_2O_5 + {}^{15}NO_2 \rightleftharpoons {}^{15}N_2O_5 + {}^{14}NO_2$$

has also been studied[40, 41]; it has a reaction rate similar to that between dinitrogen pentoxide and nitric oxide, indicating that the first step in both reactions is the same. A falling off of the first-order rate constant at very low pressures has been predicted and discussed in relation to earlier work, and the limiting high pressure value for the initial step in the decomposition has been given.[42]

A recently proposed scheme for reactions involving dinitrogen pentoxide is given below.[43] This series of reactions covers the decomposition of dinitrogen pentoxide,

Refs. p. 274

the decomposition in the presence of nitric oxide, the decomposition of ozone in the presence of dinitrogen pentoxide and the formation of dinitrogen pentoxide from ozone and nitrogen dioxide.

$$\begin{gathered}
N_2O_5 + M \rightarrow N_2O_5^* + M \\
N_2O_5^* + M \rightarrow N_2O_5 + M \\
N_2O_5^* \rightarrow NO_2 + NO_3 \\
NO_2 + NO_3 \rightarrow N_2O_5^* \\
NO_2 + NO_3 \rightarrow NO + NO_2 + O_2 \\
NO + NO_3 \rightarrow 2NO_2 \\
NO_2 + O_3 \rightarrow NO_3 + O_2 \\
NO_3 + NO_3 \rightarrow 2NO_2 + O_2
\end{gathered}$$

The photochemical decomposition of dinitrogen pentoxide has been studied and discussed[44–47] and more recent results[47] show that Norrish's mechanism[45] is acceptable:

$$\begin{gathered}
NO_2 + h\nu \rightarrow NO_2^* \\
NO_2^* + NO_2 \rightarrow 2NO + O_2 \\
2NO + 2N_2O_5 \rightarrow 6NO_2
\end{gathered}$$

Ionization in the gas-phase decomposition of dinitrogen pentoxide has been examined.[48]

The velocity of decomposition of dinitrogen pentoxide in inert solvents has been found to be similar to that in the gas phase,[49] although the rate is greater in concentrated solutions than in dilute solutions while still remaining 'unimolecular'.[50] As is to be expected, the rate is markedly different in solvents such as nitric acid where it is found to be very slow.[51]

The equilibrium:

$$N_2O_5 \rightleftharpoons N_2O_4 + \tfrac{1}{2}O_2$$

at pressures of oxygen up to 1000 atm., was found to lie entirely to the right,[52] within the experimental accuracy.

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REACTIONS OF DINITROGEN PENTOXIDE

Reaction with Nitric Oxide

The main features of the reaction $NO + N_2O_5 \rightarrow 3NO_2$ have already been dealt with (see p. 273). The mechanism originally suggested for the reaction was[1]:

$$N_2O_5 \rightleftharpoons NO_2 + NO_3$$

$$NO + NO_3 \rightarrow 2NO_2 \text{ (rapid)}$$

The overall reaction is very rapid and the velocity constant has been measured by several investigators.[1–7] Clearly, the initial rate of the reaction is that of the decomposition of dinitrogen pentoxide. The effect of inert gases has been studied,[8–10] and the results have been discussed.[11]

The data may be analysed in terms of the equations:

$$N_2O_5 + M \xrightarrow{k_1} N_2O_5^* + M$$

$$N_2O_5^* + M \xrightarrow{k_2} N_2O_5 + M$$

$$N_2O_5^* \rightarrow NO_2 + NO_3$$

$$NO_2 + NO_3 \rightarrow N_2O_5^*$$

$$NO_3 + NO \xrightarrow{k_3} 2NO_2$$

In a recent paper values are given for the constant k_1, and also for the ratio k_2/k_3.[7] (k_1 at 57 mm. pressure was found to be $10^{13\cdot 1}e^{-20\cdot 0/RT}$ sec.$^{-1}$ with k_2/k_3 under the same conditions $10^{-3\cdot 2}e^{2\cdot 3/RT}$.)

Reactions with Ozone and Oxygen

The rapid reaction $N_2O_5 + O_3 \rightarrow 2NO_2 + 2O_2$ has not been examined recently, but it is of interest that earlier workers had suggested that the species NO_3 should be considered to participate in the reaction scheme,[25–28] and that participation of this species is indicated by certain spectroscopic evidence.[12]

Refs. p. 277

It has been noted that ozone and nitrosyl chloride do not react to form nitryl chloride in the absence of dinitrogen pentoxide. In the presence of the pentoxide possible reactions are[13]:

$$N_2O_5 \rightarrow NO_2 + NO_3$$
$$NO_2 + NO_3 \rightarrow N_2O_5$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NOCl + NO_3 \rightarrow NO_2Cl + NO_2$$

The corresponding scheme for the interaction of dinitrogen pentoxide and ozone is clear from the sub-section on the decomposition of dinitrogen pentoxide (p. 272).

Flame propagation in the system dinitrogen pentoxide and ozone has been examined,[14–17] and the colour of the flame has been attributed to the formation of NO_3.

Oxygen enriched with ^{18}O has been shown to undergo isotopic exchange with dinitrogen pentoxide, the suggested scheme[18] being:

$$N_2O_5 \rightarrow NO_2 + NO_3$$
$$NO_3 + NO_2 \rightarrow N_2O_5$$
$$NO_2 + O_2 \rightarrow NO_4$$
$$NO_4 \rightarrow NO_2 + O_2$$
$$N^{18}O_4 + NO_3 \rightleftharpoons N^{18}O_3 + NO_4$$

The new species, NO_4, is tentatively regarded as having a peroxy linkage.[18]

Preparation of Nitronium Salts from Dinitrogen Pentoxide

Recently an excellent paper[19] on the isolation of nitronium salts has established the following reactions:

$$N_2O_5 + 3HClO_4 \rightarrow 2(NO_2^+)(ClO_4^-) + (H_3O^+)(ClO_4^-)$$
$$2N_2O_5 + (H_3O^+)(ClO_4^-) \rightarrow (NO_2^+)(ClO_4^-) + 3HNO_3$$

It has also been found that pure nitronium pyrosulphate can be prepared by heating dinitrogen pentoxide (1 mol.) with less than 2 mol. of sulphur trioxide:

$$N_2O_5 + 2SO_3 \rightarrow (NO_2^+)_2(S_2O_7^{--})$$

though the existence of the compound $N_2O_5,4SO_3$ could not be confirmed.

Reactions with the two halosulphonic acids are of interest and are different. Nitronium fluorosulphonate results from the interaction of dinitrogen pentoxide and fluorosulphonic acid

$$N_2O_5 + F.SO_3H \rightarrow (NO_2^+)(F.SO_3^-) + HNO_3$$

but with chlorosulphonic acid the ions of this salt apparently interact to yield nitryl chloride as one of the products:

$$N_2O_5 + Cl.SO_3H \rightarrow (NO_2^+)(ClSO_3^-) + HNO_3$$
$$HNO_3 + (NO_2^+)(Cl.SO_3^-) \rightarrow NO_2Cl + (NO_2^+)(HSO_4^-)$$
$$2(NO_2^+)(HSO_4^-) \rightarrow (NO_2^+)(HS_2O_7^-) + HNO_3$$

There is a side reaction giving as by-products chlorine and dinitrogen tetroxide, for which various equations have been written.

The compound $4SO_3,N_2O_5,3H_2O$ has been reported from phase diagram studies,[20] and later two additional phases have been found, namely $6SO_3,N_2O_5,2H_2O$ and the compound mentioned above, $4SO_3,N_2O_5$. From the study of Raman spectra it has been suggested[22] that the compound $N_2O_5,3SO_3$ may be written $(NO_2^+)_2(S_3O_{10}^{--})$ as indicated previously.[19]

Miscellaneous Reactions

The reaction between dinitrogen pentoxide and sodium fluoride has been suggested as a suitable means of preparing nitryl fluoride[23]:

$$NaF + N_2O_5 \rightarrow NaNO_3 + FNO_2$$

The reported formation of a compound between dinitrogen pentoxide and silicon tetrafluoride has not been confirmed.[24]

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SECTION XXIX

THE PRODUCTION OF NITRIC ACID

BY R. G. HALFORD

The development of the catalytic production of ammonia from nitrogen and hydrogen (see Volume VIII, Supplement I, p. 259) has provided a cheap source of nitrogen for nitric acid manufacture. Coupled with developments in materials of construction and equipment, this fact has resulted in the virtual disappearance of the manufacture of nitric acid from sodium nitrate.

The essential reactions in the formation of nitric acid from ammonia are given below:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$2NO_2 \rightleftharpoons N_2O_4$$
$$3N_2O_4 + 2H_2O \rightleftharpoons 4HNO_3 + 2NO$$

These reactions are discussed below and their influence upon nitric manufacture assessed. The extensive patent literature on this subject has not been considered.

THE REACTION $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

This reaction is catalysed by platinum-type catalysts but thermodynamically the formation of nitrogen, rather than nitric oxide, is favoured. Possible reactions are:

$$\begin{aligned}
4NH_3 + 5O_2 &\rightarrow 4NO + 6H_2O + 21{\cdot}46 \text{ kcal.}\\
4NH_3 + 3O_2 &\rightarrow 2N_2 + 6H_2O \ + 30{\cdot}28 \text{ kcal.}\\
4NH_3 + 6NO &\rightarrow 5N_2 + 6H_2O \ + 47{\cdot}64 \text{ kcal.}\\
2NH_3 &\rightleftharpoons N_2 + 3H_2 \quad - 22{\cdot}00 \text{ kcal.}\\
4NH_3 + 7O_2 &\rightarrow 4NO_2 + 6H_2O\\
NH_3 + 2O_2 &\rightarrow HNO_3 + H_2O
\end{aligned}$$

Harrison and Kobe[1] have obtained the free-energy changes of these main reactions as a function of temperature. The equilibrium constants (in terms of gas pressures) for the formation of the compounds indicated from 1 mole of ammonia are listed in Table I.

Table I.—Equilibrium Constants for the Formation of Various Compounds from 1 *mole of Ammonia*

T°K.	N_2(g)	N_2O(g)	NO(g)	NO_2(g)	HNO_3(g)
300	$7{\cdot}33\times10^{56}$	$7{\cdot}30\times10^{47}$	$6{\cdot}39\times10^{41}$	$7{\cdot}68\times10^{47}$	$6{\cdot}30\times10^{28}$
500	$7{\cdot}06\times10^{34}$	$4{\cdot}44\times10^{28}$	$1{\cdot}13\times10^{26}$	$1{\cdot}43\times10^{28}$	$1{\cdot}32\times10^{14}$
700	$2{\cdot}61\times10^{25}$	$2{\cdot}69\times10^{20}$	$2{\cdot}11\times10^{19}$	$5{\cdot}04\times10^{19}$	
900	$1{\cdot}49\times10^{20}$	$7{\cdot}36\times10^{15}$	$3{\cdot}80\times10^{15}$	$9{\cdot}94\times10^{14}$	
1100	$6{\cdot}71\times10^{16}$	$9{\cdot}12\times10^{12}$	$1{\cdot}54\times10^{13}$		
1300	$3{\cdot}18\times10^{14}$	$8{\cdot}85\times10^{10}$	$3{\cdot}36\times10^{11}$		
1500	$6{\cdot}19\times10^{12}$	$2{\cdot}95\times10^{9}$	$2{\cdot}00\times10^{10}$		

To increase the efficiency of nitric oxide formation the reaction is caused to take place at high temperatures and with rapid passage of gas through the catalyst.

A large amount of experimental work[2–10] has established a number of facts about the nature of the reaction. It has been shown that:

(*a*) there is an optimum temperature for the conversion for any given contact time, and as the contact time is decreased the optimum temperature increases.

(*b*) at low flow-rates the counter-current diffusion of gases is an important factor.

(*c*) at high flow-rates reactions which take place after the catalyst become more important owing to the passage of excess of ammonia through the catalyst.

(*d*) at certain flow-rates losses of nitric oxide are incurred when the first intermediate product can react with ammonia to give nitrogen.

(*e*) it is essential to distinguish between successive and simultaneous reactions.

(*f*) a large number of intermediates have been isolated: hydroxylamine, hydrazine, nitric oxide, nitric acid, nitrous acid, nitrous oxide.

The reaction mechanism is not known with certainty and there is a difference of opinion as to which reaction product is first formed. Some of the possible mechanisms are discussed below.

HYDROXYLAMINE THEORY[7, 8]

Bodenstein indentified hydroxylamine as an intermediate product and suggested the following mechanism:

Reactions to give NO:

$$\begin{aligned} NH_3+O &\rightarrow NH_2OH \\ NH_2OH+O_2 &\rightarrow HNO_2+H_2O \\ HNO_2+O_2 &\rightarrow HNO_4 \\ HNO_4 &\rightarrow NO+O_2+OH \\ 2OH &\rightarrow H_2O+O \end{aligned}$$

Reactions to give N_2O:

$$\begin{aligned} NH_2OH+O &\rightarrow HNO+H_2O \\ 2HNO &\rightarrow N_2O+H_2O \end{aligned}$$

Reactions to give N_2:

$$\begin{aligned} HNO_2+NH_3 &\rightarrow 2H_2O+N_2 \\ HNO+NH_2OH &\rightarrow 2H_2O+N_2 \end{aligned}$$

Under optimum conditions the atomic oxygen[11] formed on the catalyst surface reacts with ammonia to give first hydroxylamine and then nitric oxide and water. Under non-optimum conditions the hydroxylamine diffuses from the surface into the gas phase, where elemental nitrogen is formed. With very high temperatures and long contact times this takes place in front of the catalyst (diffusion of hydroxylamine against the gas stream), but with low temperatures and short contact times it takes place after the catalyst.

NITROXYL THEORY[3, 9]

Andrussov proposed the reaction of ammonia with molecular oxygen to form HNO:

$$\begin{aligned} NH_3+O_2 &\rightarrow HNO+H_2O \\ HNO+O_2 &\rightarrow HNO_3 \\ 4HNO_3 &\rightarrow 2H_2O+4NO+3O_2 \\ HNO+NH_3 &\rightarrow N_2+H_2O+H_2 \\ H_2+\tfrac{1}{2}O_2 &\rightarrow H_2O \end{aligned}$$

This mechanism assumes the adsorption of molecular oxygen, in contradiction to Langmuir's work[11] which showed the oxygen adsorbed to be in the atomic form. Furthermore the characteristic high velocity of the reaction implies that nearly every ammonia molecule that strikes the surface is converted into nitric oxide and the activation energy of a molecular reaction would be too high to allow this.

IMIDE THEORY[10]

Zawadzki reviewed the various theories and suggested that the facts are more in accord with the formation of an intermediate imide, NH.

Reactions to give NO:
$NH_3 + O \rightarrow NH + H_2O$
$NH + O_2 \rightarrow HNO_2$
$HNO_2 \rightarrow NO + OH$
$2OH \rightarrow H_2O + O$
or
$2HNO_2 \rightarrow NO + NO_2 + H_2O$
$HNO_2 + O_2 \rightarrow HNO_4$
$HNO_4 \rightarrow NO + O_2 + OH$
$2OH \rightarrow H_2O + O$

Reactions to give N_2O:
$NH + O \rightarrow HNO$
$2HNO \rightarrow N_2O + H_2O$

Reactions to give N_2:
$NH + NH_3 \rightarrow N_2H_4$
$NH + NH \rightarrow N_2 + H_2$
$NH_3 + HNO_2 \rightarrow N_2 + 2H_2O$
$2NO \rightarrow N_2 + O_2$

Oele[12] has considered the theory from the technological point of view. The characteristic volume concentrations for ammonia–air mixtures are:

Lower explosion limit at 1 atm.	13·8% NH_3 in mixture
Lower explosion limit at 5 atm.	13·0% NH_3 in mixture
Stoicheiometric composition	14·2% NH_3 in mixture
Composition at which collision chances are in the ratio $O_2:NH_3 = 5:4$	12·7% NH_3 in mixture

With an initial ammonia concentration of 10–12% the oxygen excess is low but the excess increases as decomposition proceeds. The oxygen excess is the rate-determining factor. To the first approximation it can be regarded as a stationary diffusion process in laminar flow. The mass transfer coefficient is given by:

$$\alpha = 1{\cdot}027 P^{-1} C_p^{-1} U$$

where P = total pressure, and U is the heat transfer coefficient.

Table II[12] gives results of calculations made with this formula for three closely packed gauzes of 60 μ wire diameter and 1024 meshes per cm². The overall bed depth was assumed to be three times the mesh width and the ammonia concentration to be 11% by volume.

Table II.—Effect of Conditions on Efficiency of Oxidation of Ammonia

Total pressure atm. abs.	Logarithmic mean driving force for 98% conversion atm. NH_3	Gas load per sq. metre gauze surface kg./sec.m^2	Ammonia transfer coefficient α k.mol./m.^{2} sec. atm. NH_3	Contact time 10^{-3} sec.	Calculated conversion k.mol./sec. m.^{2}	Require conversion k.mol./sec. m.^{2}
0·98	0·028	0·20	18×10^{-3}	21·6	$1{\cdot}68\times10^{-3}$	$0{\cdot}82\times10^{-3}$
		0·40	23×10^{-3}	10·8	$2{\cdot}12\times10^{-3}$	$1{\cdot}64\times10^{-3}$
		0·60	26×10^{-3}	7·2	$2{\cdot}43\times10^{-3}$	$2{\cdot}46\times10^{-3}$

In the case of atmospheric combustion a gas load of 0·50 kg. of mixture per sec. per m.^{2} of gauze surface must be used to reach at least 98% efficiency.

Burner Stability

Fig. 1 illustrates the conditions of stable combustion. The full line is a plot of the amount of heat carried away against the gauze temperature and is approximately linear. The dotted line represents the heat produced by the reaction. In the higher temperature range the line is essentially horizontal because the diffusion-controlled rate is less sensitive to temperature variation. In the lower temperature range the line tends to the *T*-axis because chemical reaction becomes rate-determining.

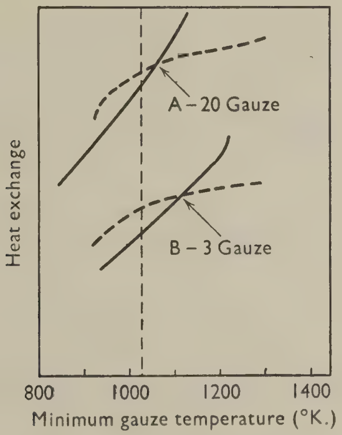

FIG. 1.—Temperature sensibility of ammonia burner elements

The point of intersection corresponds to the temperature established on the gauze. The lower point *B* holds for a three-gauze burner operated at a low gas load of about 0·40 kg./m.^{2} sec. Point *A* holds for a 20-gauze burner working at a high gas load. Point *A* is nearer to the unstable region and is ascribed to the increased effect of the reaction rate. If the line for heat removal moves further up the line for heat evolution the gauze may be 'blown cold'. The burner may be stabilized by increasing the preheat temperature or increasing the ammonia content of the reaction mixture.

Preheating

Fig. 2 illustrates the relationship between the ammonia concentration and the preheating temperature. The preheating temperature necessary to obtain stable combustion lies in the range enclosed by curves I and II.

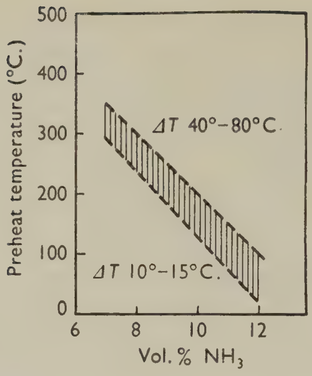

FIG. 2.—Preheating temperature for different conditions of ammonia concentration and gas load

ΔT is the temperature gradient across the catalyst pad.

Catalyst

All surfaces catalyse the oxidation of ammonia but some tend to catalyse the reaction which affords nitrogen rather than nitric oxide to such an extent as to make them non-commercial. Because of the high temperature necessary for efficient conversion the catalyst will deteriorate rapidly and as a result two classes of catalyst have been used:

(*a*) Metallic—platinum and platinum alloys[13]
(*b*) Oxides—iron oxide promoted with bismuth oxide.[14]

Catalysts of the second class have a low efficiency and in general are not used.

When a new platinum gauze is put into use the surface dulls and cauliflower-like exudations can be seen under the microscope and in this state the catalyst is highly active.

Pure platinum has an appreciable vapour pressure at the reaction temperature, and to prevent volatilization an alloying element such as rhodium is added to the catalyst.

Table III.—Efficiency of Platinum-Rhodium Alloys in Oxidation of Ammonia

Pt %	Rh %	Catalyst loss troy ounces per 10^5 lb. NH_3	Conversion efficiency %
100	0	0·903	96·1
99·5	0·5	0·776	95·5
99	1·0	0·892	97·2
98·5	1·5	0·892	97·1
98	2·0	0·766	98·3
90	10·0	0·596	99·3
85	15·0	0·608	99·6
80	20·0	0·579	99·0
50	50·0	0·563	97·0

Temperature = 900°C; 10·5 – 11·0% NH_3 in mixed gas.

Other alloying metals either have a deleterious effect or increase the catalyst loss.

Increases in platinum loss result from the change in surface of the gauze but there is no definite conclusion as to the cause. The platinum losses can constitute a reasonable proportion of the cost of the process; they can vary from 40 to 400 mg. per ton of nitric acid in atmospheric plants and in pressure operated plants may increase sevenfold.

A 100°C. rise in temperature increases the losses tenfold. This illustrates the necessity to maintain a low operating temperature and small temperature gradient across the catalyst pad. The losses per unit surface area can be related generally to the gas load by:

$$L = F\left(\frac{P^{\circ}_{\mathrm{NH_3}}}{P^{\circ}_{\mathrm{O_2}}}, G, T\right)$$

The temperature effect within the above function upon catalyst loss is expressed by the factor:

$$10^{-20{,}000/T} \text{ in the range 825–900°C.}$$

The influence of the gas load G is unknown and the ammonia/oxygen ratio is another obscure factor in platinum loss.

THE REACTION $2NO + O_2 \rightarrow 2NO_2$

This reaction has two distinctive properties[15, 16]:

(*a*) it is kinetically of third order;

(*b*) the velocity constant decreases with increasing temperature.

Three principal reaction mechanisms have been advanced:

TRIPLE COLLISION

On the kinetic theory it is difficult to define a triple collision and Bodenstein[16] suggested that the relative frequencies of ternary and binary collision were in the ratio of the molecular diameter to the mean free path. The reaction must have a low activation energy and a finite duration to every encounter. This mechanism has been developed further.[17–19]

TRANSITION STATE MECHANISM

A mechanism based upon the Transition State Theory was developed by Gershinowitz and Eyring[20] who assumed a structure for the activated complex approximating to nitrogen tetroxide.

BIMOLECULAR MECHANISM

A mechanism involving a series of bimolecular steps has been suggested:

$$2NO \rightleftharpoons (NO)_2 \qquad \ldots \text{(i)}$$

$$(NO)_2 + O_2 \rightarrow 2NO_2 \qquad \ldots \text{(ii)}$$

$(NO)_2$ has been detected by physical methods.

Reaction (i) is an equilibrium which is rapidly established, and which has an equilibrium constant K. Reaction (ii) is rate-determining and has a velocity constant k_1

$$\frac{\mathrm{d}[NO_2]}{\mathrm{d}t} = Kk_1[NO]^2[O_2]$$

The temperature dependence is attributed to a decrease in the product Kk_1 with increase in temperature.

An alternative mechanism assumes NO_3 to be the intermediate compound:[21]

$$NO + O_2 \rightleftharpoons NO_3$$

$$NO_3 + NO \rightarrow 2NO_2$$

THE REACTION $3N_2O_4+2H_2O \rightleftharpoons 4HNO_3+2NO$

This reaction is the overall reaction for the absorption of nitrous gases to give nitric acid. As will be discussed later the reaction is more complex than this equation suggests. The variation of the equilibrium constant with temperature has been calculated.[22]

$$K = \frac{(NO_2)^3(H_2O)}{(HNO_3)^2(NO)}$$

Table IV.—Variation with Temperature of the Equilibrium Constant for the Reaction $3NO_2+H_2O \rightleftharpoons 2HNO_3+NO$

T°K.	K. atm.
275	$3{\cdot}78\times10^{-2}$
293·1	$1{\cdot}37\times10^{-2}$
298·1	$1{\cdot}05\times10^{-2}$
300	$9{\cdot}51\times10^{-3}$
325	$2{\cdot}83\times10^{-3}$
350	$1{\cdot}01\times10^{-3}$
375	$4{\cdot}11\times10^{-4}$
400	$1{\cdot}87\times10^{-4}$
425	$9{\cdot}18\times10^{-5}$
450	$4{\cdot}86\times10^{-5}$
475	$2{\cdot}77\times10^{-5}$
500	$1{\cdot}65\times10^{-5}$

The practical significance of the equilibrium is shown in Fig. 3. It will be seen that a degree of oxidation of over 0·8 is needed for the preparation of 55% nitric acid from a gas having a partial pressure of nitrous gases of 0·1 atm. The favourable effect of increase of pressure on the attainable acid concentration is clear.

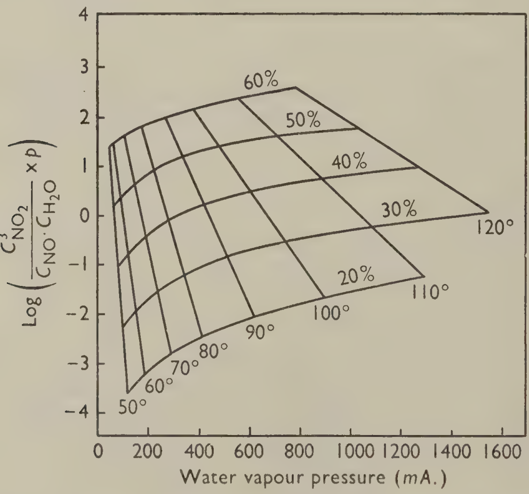

FIG. 3.—Dew points of NO—NO_2—H_2O gas mixtures

The Absorption of Nitrous Gases

The absorption of nitrous gases is usually carried out in a packed or plate tower. For efficient and economical operation it is necessary to know the mechanism of the absorption of the nitrous gases into water or dilute nitric acid, so as to form a theoretical basis for the design of the absorption system. So far the design has been based upon semi-empirical methods because there is not complete understanding of the various processes which control the reaction. Consequently a large amount of experimental work has been carried out to determine the kinetics and mechanism of the absorption reactions.

Burdick and Freed[23] bubbled nitrogen dioxide diluted with 90–95% of nitrogen through nitric acid at constant temperature and analysed the issuing gases for nitric oxide and nitrogen dioxide. They suggested that the important reactions were limited to two:

$$2NO + O_2 \rightarrow 2NO_2 \qquad \ldots \text{(i)}$$

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \qquad \ldots \text{(ii)}$$

Reaction (ii) is the fundamental reaction and is reversible. Lewis and Edgar[24] found the partial pressures of nitric oxide and nitrogen dioxide to be 1 and 10^{-5} atm. respectively with 1·1% nitric acid and Foerster and Koch[25] found the partial pressures to be 10^{-7} and 1 atm. respectively with 65·3% nitric acid. With dilute nitric acid the absorption progresses substantially to completion with the liberation of one-third of a volume of nitric oxide, whereas in concentrated nitric acid the presence of minute quantities of nitric oxide inhibits the reaction.

The equilibrium constant[23] of the reaction,

$$K_e = \frac{P_{NO}P^2_{HNO_3}}{P^3_{NO_2}.P_{H_2O}} = K_1K_2$$

where $K_1 = P_{NO}/P^3_{NO_2}$ and $K_2 = P^2_{HNO_3}/P_{H_2O}$.

Since K_2 involves only the partial pressures of water and nitric acid vapours over the solution the experimental problem lies in the determination of a series of partial constants K_1 at different concentrations and temperatures.

In the presence of oxygen at concentrations such as those met with in the gases from ammonia oxidation, the rate of reoxidation of nitric oxide is slower than the rate of absorption, with the result that the nitrous gases are always in equilibrium with the liquid. Burdick and Freed[23] calculate the percentage of nitrogen dioxide in contact with a given solution at a given temperature. From Table V it can be seen that the maximum concentration of nitric acid obtainable by water absorption is ~66·7% and that the conversion is at a maximum when a high concentration of nitrogen peroxide is absorbed in dilute nitric acid.

Chambers and Sherwood[26] point out that the above data for K_e differ by a factor of ten from their data and from those obtained by Abel *et al.*[27]. They suggest that equilibrium was not attained in the experiments of Burdick and Freed, and that the general mechanism is as follows:

(*a*) The diffusion of nitrogen dioxide in the gas phase through the surface gas film at the interface boundary.

(*b*) Diffusion of nitrogen dioxide in the liquid phase from the gas–liquid interface to the point in the liquid where the formation of nitrous acid occurs.

(*c*) Nitrous acid decomposition with the liberation of nitric oxide.

(*d*) Return of nitric oxide to the gas phase or its oxidation in the liquid phase by diffusing oxygen.

Using a wetted-wall column with gas and solution running counter-current they measured the rate of disappearance of nitrogen dioxide from calculations on the gas flow and gas analyses. With the proposed diffusion limitation in mind they made additional measurements of the gas film characteristics of the experimental apparatus, using the absorption of ammonia and sulphur dioxide into water as standards of comparison. They measured the effects of varying acid strength and gas flow rate on the absorption rate of NO_2 but maintained an almost constant gas composition throughout the test.

Table V.—Percentage Conversion of Nitrogen Peroxide to Nitric Acid by Absorption in Aqueous Solutions of Nitric Acid at 1 *atm. pressure*[23]

Conc. HNO_3 % by wt.	Temp. °C.	% NO_2 in gas								
		0·1	0·6	1·0	2·0	4·0	6·0	8·0	10·0	20·0
5	10	59·8	64·5	65·1	65·7	66·1	66·2	66·3	66·3	66·4
	25	57·1	63·3	64·4	65·3	65·7	65·9	66·1	66·2	66·3
	50	48·8	60·0	61·8	63·7	64·8	65·2	65·4	65·6	66·0
	75	32·6	53·0	56·8	60·2	62·7	63·6	64·2	64·6	65·3
10	10	54·0	62·5	63·6	64·9	65·5	65·7	65·9	66·0	66·2
	25	47·0	59·8	61·6	63·6	64·7	65·1	65·4	65·6	66·0
	50	27·8	52·2	56·0	60·1	62·3	63·5	64·1	64·5	65·3
	75	7·8	37·0	44·3	53·0	57·2	58·8	60·8	62·0	63·1
15	10	48·0	60·3	61·6	64·0	64·8	65·2	65·4	65·6	66·0
	25	35·6	55·8	58·7	61·7	63·5	64·1	64·7	65·0	65·5
	50	14·9	43·9	49·8	56·2	59·4	61·2	62·3	63·0	64·3
	75	2·4	24·2	32·6	44·0	51·5	55·0	57·1	58·4	61·5
20	10	40·0	57·0	59·2	62·3	63·8	64·5	64·8	65·1	65·7
	25	26·3	51·3	55·0	59·4	62·1	63·1	63·7	64·2	65·0
	50	6·3	34·5	42·1	51·4	56·2	58·6	60·0	61·0	63·1
	75	0·7	13·1	21·7	35·0	44·4	49·0	52·0	54·0	58·7
25	10	31·3	53·7	57·0	60·5	62·7	63·8	64·1	64·5	63·3
	25	17·7	44·2	50·0	56·4	59·6	61·2	62·1	63·9	64·2
	50	2·2	23·7	32·4	44·8	51·2	54·6	56·4	57·7	61·3
	75	0·2	5·9	11·8	23·6	35·0	41·8	45·2	48·2	54·8
30	10	24·4	48·4	53·3	57·6	60·8	62·1	62·9	63·5	64·6
	25	7·6	35·8	43·0	51·6	56·4	58·5	60·0	60·9	62·8
	50	0·7	13·1	21·2	34·6	44·4	48·8	51·7	53·6	58·3
	75	—	2·3	5·8	14·0	25·6	32·8	38·0	41·2	49·6
35	10	14·6	41·8	47·6	53·8	57·8	59·8	61·0	61·8	63·4
	25	3·0	26·8	34·0	44·4	51·0	54·4	56·4	58·0	61·0
	50	0·3	6·3	12·3	25·6	35·8	41·8	45·2	48·2	54·8
	75	—	0·8	2·2	8·0	16·5	23·4	28·8	32·4	43·6
40	10	6·1	32·4	39·5	47·6	53·4	56·1	57·6	58·7	61·4
	25	1·0	16·3	23·0	35·4	43·5	48·0	51·0	52·6	57·6
	50	0·1	2·6	5·6	15·6	26·0	32·0	37·0	40·4	49·6
	75	—	0·3	0·8	3·4	9·0	14·4	19·6	23·4	36·2
45	10	2·2	20·4	28·2	38·0	45·8	49·7	52·0	53·5	57·6
	25	0·4	7·4	12·0	22·5	33·3	38·4	42·1	44·6	52·0
	50	—	0·8	2·1	7·2	16·6	21·6	26·0	29·6	41·2
	75	—	—	0·3	1·1	4·0	7·7	10·5	13·6	25·7
50	10	0·6	9·7	14·8	26·0	35·0	39·4	42·2	44·2	50·0
	25	—	2·8	5·0	9·6	20·8	26·6	30·7	34·3	42·0
	50	—	0·3	0·7	2·6	7·0	11·6	15·8	19·6	31·1
	75	—	—	—	0·4	1·5	3·0	4·8	6·7	15·9
55	10	—	2·7	5·2	11·5	17·9	22·0	26·2	27·7	32·6
	25	—	0·7	1·5	4·1	9·3	13·3	16·7	19·5	28·1
	50	—	—	0·2	0·9	2·8	5·0	8·4	9·4	18·9
	75	—	—	—	—	0·5	1·1	2·0	2·6	8·0
60	10	—	0·6	1·1	2·8	5·5	7·8	9·2	10.4	15·0
	25	—	—	0·2	1·0	2·6	4·1	5·8	6·8	12·2
	50	—	—	—	0·3	0·9	1·6	2·5	3·6	8·5
	75	—	—	—	—	—	0·3	0·6	0·8	1·6
65	10	—	—	0·2	0·4	0·8	1·2	1·6	1·9	3·2
	25	—	—	—	—	0·5	0·8	1·1	1·5	3·6
	50	—	—	—	—	—	—	0·6	0·8	1·5
	75	—	—	—	—	—	—	—	—	—

They found that the Gas Film Absorption coefficient was proportional to $Re^{0\cdot 8}$ (Re = Reynolds Number, $vd\rho/\eta$, where v = linear velocity, ρ = density, η = viscosity of circulating gas, and d = diameter of adsorption tower) over a wide range of acid and alkali concentrations, indicating the gas-film diffusional resistance to be controlling.

Assuming that the nitrous oxides are in equilibrium across the interface, Chambers and Sherwood[26] calculated the absorption rate to be:

$$N = \frac{P}{RTP_b x}(2D_{N_2O_4}[N_2O_4] + D_{NO_2}[NO_2])$$

where P = total pressure
P_b = mean partial pressure of inert gas in film
x = effective film thickness
D_i = diffusion coefficient of species i.

The absorption coefficients calculated from the above equation were considerably greater than those measured experimentally and the extent of the discrepancy increased with increasing acid concentration.

The authors postulated the formation of a moderately stable mist by the interaction of nitrogen dioxide and water vapour in the gaseous phase. If the partial pressure of the nitrogen dioxide in the gas is large and the vapour pressure of the water over the solution is low the mist will be deposited in a layer near the gas–liquid interface. This mist would be difficult to dissipate since that part of the gas film would be stagnant. No film of mist was observed, but mist was evident in the main body of the gas.

Denbigh and his co-workers[28] considered the process to be limited by the rate of chemical reaction rather than by diffusion. From experiments with a falling film tower they were able to show that:

(*a*) The rate of absorption of nitrogen dioxide was the greater the higher its concentration and the lower the nitric oxide concentration.

(*b*) The rate was greater at 25°C. than at 40°C.

(*c*) An increase in the acid concentration caused a decrease in the rate of absorption of the dioxide and an increase in the rate of absorption of nitric oxide.

(*d*) After circulation the solution developed a green colour and subsequent analysis showed the presence of 0·5–1·5% of nitrous acid.

(*e*) The tangent to the curve of nitric oxide concentration could be used to calculate the approximate figure for the rate of evolution of nitric oxide, which was generally less than one-third the rate of absorption of the dioxide due to the formation of nitrous acid.

(*f*) No mist was observed.

The values of K_1 obtained agreed with values obtained by other workers[26, 27, 29] but the interpretation of the results disagreed radically with that put forward by Chambers and Sherwood.

Denbigh *et al.*[28] point out that Chambers and Sherwood's assumption that the rate of absorption was proportional to the area of acid surface did not indicate the nature of the rate-limiting process, and further that any expression for the rate of absorption must reduce to zero when the composition of the gaseous phase is that which is in equilibrium with the acid. Chambers and Sherwood's equation does not do this. Furthermore, no allowance was made for the considerable effect of nitric oxide on the absorption rate. With dilute acid, where the reverse reaction is negligible, the equation does not correctly express the effect of the concentration of the dioxide and tetroxide on the absorption rate. Chambers and Sherwood could not check if their theoretical equation was in agreement with experiment since their experimental work was carried out with a constant gas composition.

Denbigh and Prince[28] suggest that the rate-limiting process is the chemical reaction involving nitrogen dioxide or tetroxide or both simultaneously.

They assumed the same elementary reactions as Abel[30]:

$$
\begin{array}{lr}
4HNO_2 \rightleftharpoons 2NO + 2NO_2 + H_2O & (a) \\
N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2 & (b) \\
3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O & \text{overall} \\
2N_2O_4 + 2H_2O \rightleftharpoons 2HNO_3 + 2HNO_2 & (b) \\
2HNO_2 \rightleftharpoons NO + NO_2 + H_2O & (a) \\
3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO & \text{overall } (c)
\end{array}
$$

They agreed with Abel that reaction (*b*) is rate-determining, thus giving the rate in dilute acid proportional to (N_2O_4) and the rapid development of the steady state of coloration corresponding to reaction (*a*).

On their basis the rate of absorption per unit area was expressed as:

$$V = k_a\{[N_2O_4] - C[N_2O_4]^{1/4}[NO]^{1/2}\}$$

Caudle and Denbigh[28] extended this work using more refined techniques and found the absorption process more complex than had hitherto been thought.

The rate of absorption (expressed as equivalent moles of NO_2 absorbed per unit area of interfacial surface) was found to be proportional to the concentration of nitrogen dioxide provided that the nitric oxide content is low. The relationship must be modified when there is an appreciable amount of nitric oxide in the gas:

$$R_{NO_2} = b[N_2O_4] + c[N_2O_3]^n$$

$$
\begin{array}{ll}
\text{At } 25°\text{C., } & b = (1{\cdot}92 \times 10^{-3}) Re_{\text{gas}}{}^{0{\cdot}74} Re_{\text{liquor}}{}^{0{\cdot}22} \text{ cm. sec.}^{-1} \\
35°\text{C., } & b = (1{\cdot}74 \times 10^{-2}) Re_{\text{gas}}{}^{0{\cdot}56} Re_{\text{liquor}}{}^{0{\cdot}20} \text{ cm. sec.}^{-1} \\
45°\text{C., } & b = (2{\cdot}50 \times 10^{-1}) Re_{\text{gas}}{}^{0{\cdot}22} Re_{\text{liquor}}{}^{0{\cdot}35} \text{ cm. sec.}^{-1}
\end{array}
$$

The value of n was not determined with accuracy and may be between $\frac{1}{2}$ and 1; c had values 2 to 10 cm. sec.$^{-1}$ at 25°C., 8–20 cm. sec.$^{-1}$ at 45°C.; the *Re* values are Reynolds numbers for gas and liquor. The smallness of the second term is due to the low value of (N_2O_3) except at low gas dilutions with appreciable nitric oxide present.

As in Denbigh's previous paper an unsuccessful attempt was made to explain the experimental results on the basis of the two-film theory. The results were interpreted on the basis of chemical reaction, but modified to suggest that the reaction took place mainly at the interface. To explain the dependence of the absorption rate upon flow rate it was suggested that the chemical reaction does not take place to an equal extent on all parts of the gas–liquid interface. An infinite set of sub-areas of varying absorption capacity was envisaged, the absorption capacity of each sub-area depending upon the flow-rate.

Peters *et al.*[31] support the presence of a gas phase reaction and postulate the following mechanism: Some of the gaseous nitrogen dioxide and tetroxide reacts with water vapour in the gas film to form nitric and nitrous acid. Most of the nitric acid diffuses into the liquid phase and some water and nitric acid condense in the form of a mist. Part of the nitrous acid decomposes in the vapour phase to give nitric oxide, nitrogen dioxide and water and the remainder diffuses into the liquid to undergo the same decomposition. Some of the nitrogen dioxide and tetroxide diffuses into the liquid phase before reacting with the water.

The experimental facts did not support the diffusion theory as proposed by Chambers and Sherwood. An attempt based upon combined diffusional resistance and rate of chemical reaction as controlling factors according to a method derived by Hatta[32] was equally unsuccessful.

It was concluded, therefore, that chemical reaction in the gas phase is the rate-controlling factor.

Assuming that Abel's[30] equations are correct, that nitrogen dioxide and nitrogen tetroxide are in continuous equilibrium and that the stationary state is rapidly attained, Peters *et al.* obtained a rate equation of the form

$$-\frac{\mathrm{d}[N_2O_4]}{\mathrm{d}t}\left(\frac{4}{3}+\frac{1}{3\sqrt{K_e[N_2O_4]}}\right) = k_1+\frac{k_3}{2K_e}[N_2O_4][H_2O]-(k_2+k_4)[HNO_2][HNO_3]$$

where k_1 and k_2 are the forward and reverse rate constants of the reaction

$$N_2O_4+H_2O \rightarrow HNO_3+HNO_2$$

and k_3 and k_4 are the forward and reverse rate constants of the reaction

$$2NO_2+H_2O \rightarrow HNO_3+HNO_2$$

The equilibrium constant $K_e=[N_2O_4]/[NO_2]^2$.

A plot of plate efficiency against percentage of nitrous gases shows an increase in efficiency with increase in nitrous gas concentration. Also an increase in pressure at any given gas composition causes a large fraction of the gases to be present as the tetroxide and to give a higher plate efficiency.

Peters and Holman[33] continued the above work and made measurements of nitrogen dioxide absorption rates into water, sodium hydroxide solution and sodium chloride solution. A pronounced rise in the gas temperature above that of the liquor occurred, showing the presence of a gas-phase reaction. This was supported by the presence of a small amount of nitric oxide in the exit gas stream with absorption into sodium hydroxide solution.

Opposed to the suggestion of a gas phase reaction providing the limiting step were the measurements showing the decreased absorption rate by sodium chloride solution. If a gas phase reaction controlled the kinetics then the rate of absorption would fall in proportion to the decrease in water vapour pressure over the salt solution. The measured rate was only 44% of the value for pure water compared with the predicted value of 79%. The authors concluded that the major proportion of the chemical reaction occurs in the region of contact between the two phases, with an appreciable amount in both the gas and liquid phases.

Peters and Koval[34] carried out further experiments with a stirred tank reactor to augment the gas–liquid contact time and area. They found an increase in efficiency as compared with the bubble tray experiments and that the equation proposed by Peters *et al.*[31] did not agree with the results obtained. Because of the increase in contact time and area further reactions may have become important and these were suggested to be:

$$NO+NO_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} N_2O_3$$

$$N_2O_3+H_2O \underset{k_6}{\overset{k_5}{\rightleftharpoons}} 2HNO_2$$

Their rate equation then became:

$$-\frac{\mathrm{d}[NO_2]}{\mathrm{d}t} = k[N_2O_4]+k'[NO][NO_2]$$

where

$$k = \frac{k_1}{K_e}+2k_2[H_2O]$$

k_1 = rate constant for reaction $2NO_2+H_2O \rightleftharpoons HNO_3+HNO_2$

k_2 = rate constant for reaction $N_2O_4+H_2O \rightleftharpoons HNO_3+HNO_2$

K_e = equilibrium constant for reaction $2NO_2 \rightleftharpoons N_2O_4$

$$k' = \frac{k_3k_5[H_2O]^2}{k_4+k_5[H_2O]^2}$$

The authors suggest that k' should be proportional to the ratio of the gas–liquid contact area to the gas volume in the reactor.

More recent work[35] has shown the existence of an appreciable gas film resistance, a liquid film resistance, and a transfer rate across the liquid film proportional to the N_2O_4 concentration in the gas in contact with the interface. These facts rationalize the apparent disagreement among other investigators,[26, 28, 31] whose results are approximations to a more complex relation.

Andrew and Hanson[36] have described four possible reaction mechanisms to predict absorption tower performances:

(*a*) Formation of nitrous acid in the gas phase, followed by its diffusion into and decomposition in the liquid phase and diffusion of nitric oxide into the gas phase.

$$\begin{aligned} &NO_2(g) + NO(g) + H_2O \rightarrow 2HNO_2(g) \\ &HNO_2(g) \rightarrow HNO_2(l) \\ &HNO_2(l) \rightarrow HNO_3(l) + NO(l) \\ &NO(l) \rightarrow NO(g) \end{aligned}$$

(*b*) Nitrogen dioxide diffuses through the gas film as the tetroxide and reacts in the liquid film to give nitric and nitrous acids. The nitric acid diffuses into the bulk liquid, and the nitrous acid diffuses into the gaseous phase.

$$\begin{aligned} &2NO_2(g) \rightleftharpoons N_2O_4(g) \\ &N_2O_4(g) \rightarrow N_2O_4(l) \\ &N_2O_4(l) + H_2O \rightarrow HNO_3(l) + HNO_2(l) \\ &HNO_2(l) \rightarrow HNO_2(g) \end{aligned}$$

(*c*) The third process is the gas phase formation of nitric acid followed by its transfer to the liquid phase.

$$\begin{aligned} &NO_2(g) + H_2O(g) \rightarrow HNO_2(g) + HNO_3(g) \\ &HNO_3(g) \rightarrow HNO_3(l) \end{aligned}$$

(*d*) The final process is the direct absorption of nitrogen tetroxide:

$$\begin{aligned} &NO_2(g) \rightarrow NO_2(l) \\ &2NO_2(l) \rightarrow N_2O_4(l) \\ &N_2O_4(l) + H_2O(l) \rightarrow HNO_3(l) + HNO_2(g) \\ &HNO_2(l) \rightarrow HNO_2(g) \end{aligned}$$

At high gas concentration, $[NO_2] > 5{\cdot}0 \times 10^{-7}$ g. mole/cm.^{3}, mechanism (*b*) is predominant.

At low gas concentration, $[NO_2]g < 0{\cdot}5 \times 10^{-7}$, the predominant mechanism is dependent on the $[NO]/[NO_2]$ ratio in the gas phase. When $[NO]/[NO_2] < 0{\cdot}5$ mechanism (*d*) predominates. With $[NO]/[NO_2] > 5{\cdot}0$ mechanism (*a*) is the most important. At intermediate concentrations all mechanisms participate.

Carberry[37] has suggested that the reaction sequence is partially ionic, evidence for which has been summarized by Gray and Yoffe.[38]

$$\begin{aligned} &2NO_2(g) \rightarrow N_2O_4(g) \\ &N_2O_4(g) \rightarrow N_2O_4(l) \\ &N_2O_4(l) \rightarrow NO^+ + NO_3^- \\ &N_2O_4 + H_2O \rightarrow H^+ + NO_3^- + HNO_2 \\ &2HNO_2 \rightarrow H_2O + NO + NO_2 \end{aligned}$$

Carberry was also able to derive an equation for the rate of absorption identical with that given by Denbigh.

THE DESIGN OF NITRIC ACID PLANTS

The design of nitric acid plants is influenced by the pressure at which the plant is to operate. The trend in America is to build plants to operate at 8 atm. In Europe economic considerations have resulted in plants being designed to operate at many pressures between 1 and 8 atm.

Pressure Oxidation Plant

The flowsheet is shown in Fig. 4 and the operation has been described.[39] The mixture of ammonia and air is passed over a multi-layer catalyst pad at a throughput per unit cross section of area ten to twenty times that of an atmospheric plant. This gives a lower conversion efficiency and a higher catalyst loss. The gases are cooled and passed through a bubble cap plate tower, which because of the increase in rate of absorption of nitrous gases is much smaller than the atmospheric absorption train.

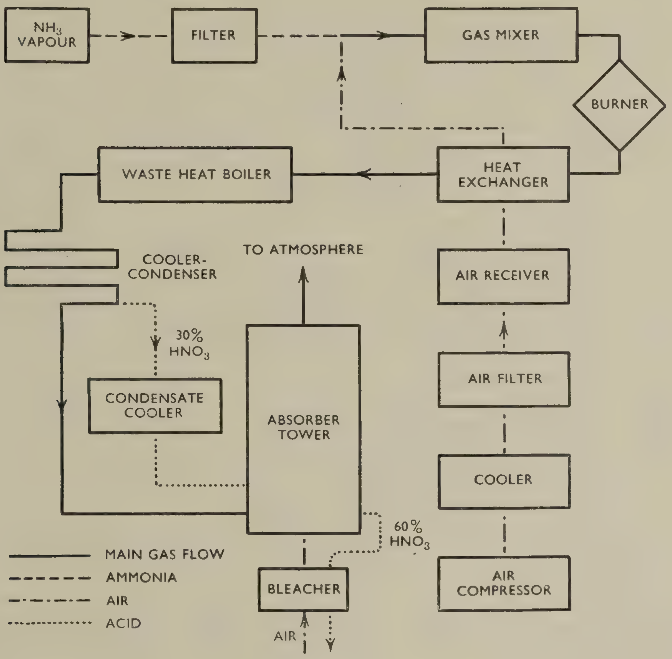

Fig. 4.—Flowsheet for 8 atmospheres nitric acid plant

Most plants are equipped with power recovery systems[40] whereby the waste gases before entering the atmosphere are passed through a turbine coupled with the compressor.

The main disadvantages of the plant are its lower conversion efficiency and high catalyst loss. Its advantages lie in the high absorption efficiency, the production of 60% acid and the low capital investment.

The Atmospheric-Pressure Plants

The flowsheet of this type of plant is shown in Fig. 5 and has been described.[41] The filtered air and ammonia are preheated in the top drum of a waste heat boiler system, filtered and allowed to pass downwards through eight burners in parallel. The heat content of the hot gases is used to raise steam and the gases then pass through seven packed towers in series. The first tower is used for cooling the gases to 50°C., the second provides an oxidation space and secondary air is admitted to it,

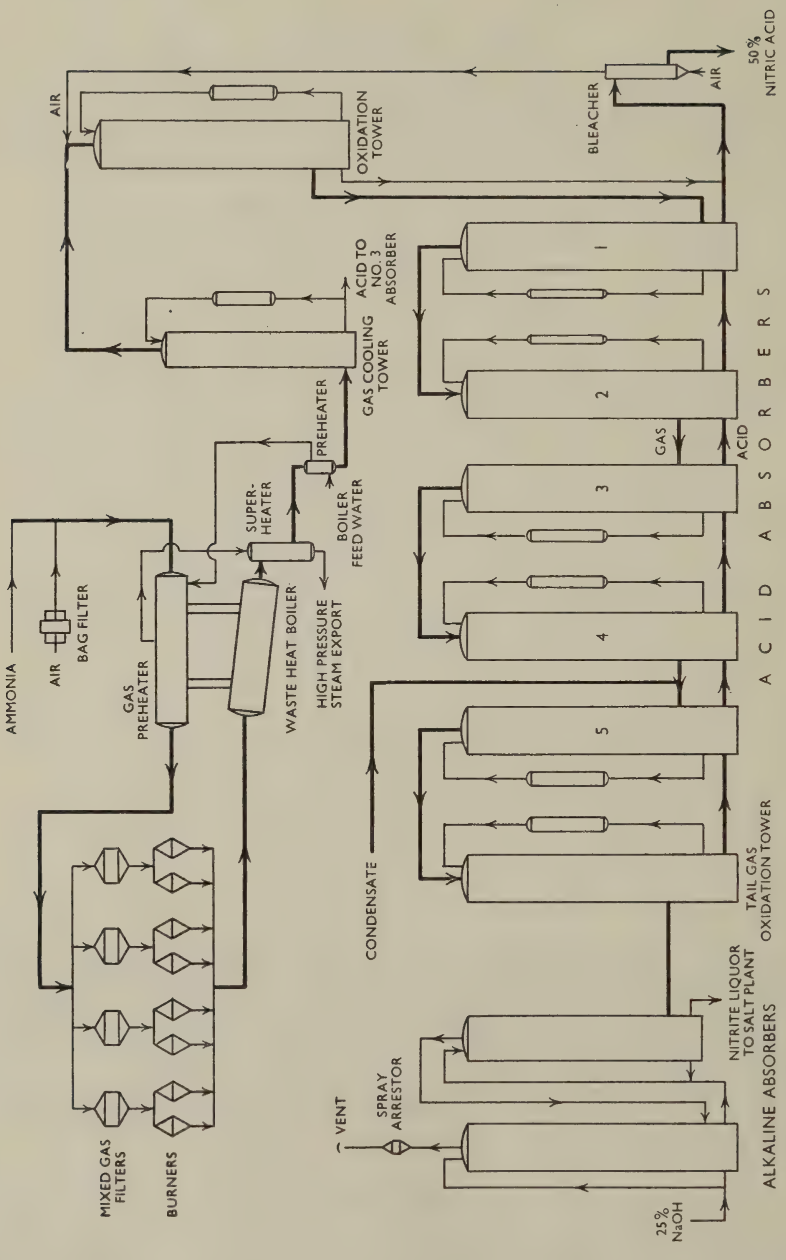

FIG. 5.—Atmospheric pressure plant for nitric acid

the remainder being the main absorption towers. In each tower the gases are scrubbed with water or acid and approximately 92% of the nitrous gases is removed. The remaining 8% is removed in three towers containing caustic soda solution and produces a mixture of sodium nitrite and sodium nitrate.

This type of plant has a higher conversion efficiency than the pressure operated plant, but requires a higher capital cost and produces 50% acid.

Combined Plant

A plant which attempts to avoid the drawbacks of the two types described above has been developed (Fig. 6). The oxidation is carried out at atmospheric pressure and the cooled gases are compressed in a stainless steel compressor followed by a bubble-cap plate tower.

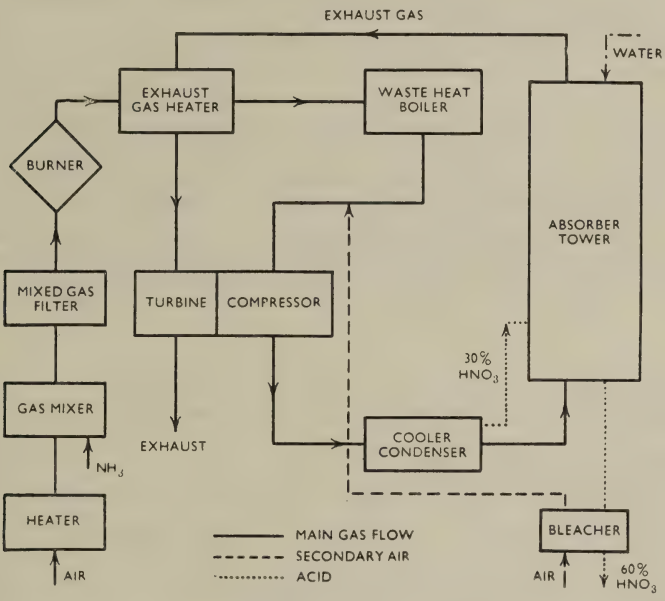

FIG. 6.—Nitric acid plant combining atmospheric pressure oxidation with high pressure absorption

Strelzoff[42] has made a critical comparison of the three types of plant and his conclusions are given in Table VI:

Table VI.—Performance of Various Types of Plant for the Production of Nitric Acid

	Atmospheric	Pressure	Combined
NH_3 tons	0·287–0·290	0·290–0·294	0·287–0·290
Platinum loss, troy oz.	0·0025	0·005–0·01	0·0025
Power K.W.H.	85–90	*350	*350
Relative Steam Credit tons	1·0	0·8–1·25	1·0
Acid Strength %	45–52	57–60	57–60
Relative Investment Cost	1·0	0·89	1·11
Alkali Sales %	5	—	—

All figures are per ton HNO_3.
* Depends on power recovery.

THE CONCENTRATION OF NITRIC ACID

Nitric acid and water form a constant boiling mixture at 68% nitric acid and therefore concentrated nitric acid cannot be prepared by direct distillation. The usual method of concentrating the acid is to remove the water with concentrated sulphuric acid.[43] The vapour–liquid equilibria of the system HNO_3–H_2O–H_2SO_4 have been obtained,[44, 45, 46] but it has been pointed out[48] that the actual performance of the equipment did not match that calculated from the equilibrium data, and redetermined data have been published.[47]

A further development in concentrating nitric acid has been the use of magnesium nitrate as desiccant.[48] A 60% solution of nitric acid and a 72% solution of magnesium nitrate at 140°C. are introduced half way up a dehydrating tower. Approximately 85% nitric acid passes to a rectifying column and a 68% magnesium nitrate solution leaves the bottom of the tower and is re-evaporated. The nitric acid is concentrated in the column to 99·5%.

The other line of development has been the direct preparation of concentrated nitric acid.[49, 50]

In the first case[49] ammonia is burnt with pure oxygen and pure nitrogen tetroxide is condensed out in a brine liquefier. The tetroxide is treated in an autoclave at 52 atm. for 4 hours with water and oxygen to give 99·9% nitric acid.

The Wisconsin process[50] passes air through a preheating bed of magnesia, and heats the air further to 2200°C. by the combustion of fuel gas. The air is kept at this temperature for three seconds and then chilled in 0·1 second. The resulting gas contains 1·0% of nitric oxide by volume which, after removal of water, is oxidized on silica gel. The resulting nitrogen dioxide is driven off and condensed as above.

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SECTION XXX

THE PHYSICAL PROPERTIES OF NITRIC ACID

BY P. E. CURRY

Density

The density of nitric acid solutions at 10°, 20° and 40° is shown in Table I.[10]

Table I.—Density of Aqueous Nitric Acid

g./ml.	% HNO_3							
	99·19	88·34	77·24	69·86	52·13	38·05	25·28	12·65
d (10°)	1·5306	1·4958	1·4612	1·4275	1·3339	1·2427	1·1555	1·0739
d (20°)	1·5108	1·4793	1·4451	1·4131	1·3222	1·2337	1·1492	1·0698
d (40°)	—	1·4468	—	1·3835	1·2982	—	1·1355	1·0603

Another series of determinations[1] over the range 73% to 99% HNO_3 is shown in Table II. Further data are available[83] for 95·90–100·000 wt.-% HNO_3 at 15°.

Table II.—Density of Aqueous Nitric Acid

% HNO_3	Density, g./ml.		
73·0	1·4460 at 5°	1·4295 at 14°	1·4115 at 28°
82·9	1·4860 at 5°	1·4652 at 18°	1·4476 at 29°
95·0	1·5200 at 4°	1·5020 at 15°	1·4750 at 20°
98·7	1·5300 at 4°	1·5130 at 15°	1·4870 at 20°

The density of solutions of NO_2 in nitric acid at 15° increases[3] from 1·5130 for 100% HNO_3 to a maximum of 1·630 at 44·2–50·7% NO_2 and then decreases to 1·6186 g./ml. for the saturated solution (55·73% NO_2). At 0°[2] as the NO_2 content ranges from 0 to 41%, the density increases from 1·5472 to 1·6727 and then falls gradually to 1·657 at 55% NO_2. At 12·5° and 25°, the maximum densities are 1·6508 and 1·6273 respectively. In the system HNO_3–NO_2, with 19 N. HNO_3 the density at 0° ranges from 1·4918 at 0% NO_2 to a maximum of 1·5256 at 14% NO_2. With 16 N. HNO_3 the density at 0° ranges from 1·4491 at 0% NO_2 to a maximum of 1·4729 at 16% NO_2. These results have been held to indicate presence of a NO_2–HNO_3 compound in the solutions.

From 1·00° to 32·33°, the density of pure nitric acid can be expressed by the equation, $d_t = 1{\cdot}5492 - 0{\cdot}00182t$ (°C.).[4] Another[5] equation is $d = (d_1 + \alpha[H_2O]) + \beta(t_2 - t_1)$ where $(d_1 + \alpha[H_2O])$ is the density at a reference temperature such as 35°, $\beta(t_2 - t_1)$ is a temperature correction term, α is a function of the N_2O_4/HNO_3 ratio, β is a function of this ratio and the water content and $d = d_1 + \alpha + \beta$.

The specific volumes of nitric acid are given in Table III.[7–8]

Table III.—Specific Volume of Nitric Acid

Pressure (p.s.i.)	Specific volume, cu. ft./lb.	
	70°F. Physical equilibrium	190°F. Physical and chemical equilibrium
200	0·010591	0·03680
400	0·010575	0·02115
600	0·010559	0·01641
800	0·010545	0·01411
1000	0·010529	0·01312
1250	0·010510	0·01237
1500	0·010494	0·01185
1750	0·010479	0·01153
2000	0·010464	0·01137
2250	0·010451	0·01127
2500	0·010439	0·01125
2750	0·010428	0·01124
3000	0·010417	0·01122
3500	0·010398	0·01121
4000	0·010380	0·01119
4500	0·010365	0·01118
5000	0·010354	0·01117

Further measurements at physicochemical equilibrium have been made in degradation studies.[9] Specific volumes have been used to determine possible hydrogen bond formations.[6]

The density of white fuming nitric acid at 25° is 1·494 g./ml. with 97·08% HNO_3.[11–12] In the HNO_3–NO_2–H_2O system[13] the density increases with NO_2 concentration and decreases with H_2O concentration. At 0° a maximum occurs at 45 w/w% NO_2. This may be due to formation of NO_3^- ions by ionization of NO_2 in the nitric acid followed by association with the HNO_3 to form $(HNO_3)_2,NO_3^-$ ions. The specific volume of red fuming nitric acid[15] is 0·01063 cu. ft./lb. at 130°F. and 100 p.s.i.

The density of aqueous solutions of deuterium nitrate, DNO_3, is given in Table IV.[14]

Table IV.—Density of Deuterium Nitrate Solutions

Concentration (g./100 g. of water)	4·606	8·507	11·971	16·263	19·34	22·91	26·05	33·76	40·02	46·02	52·76
d^{20}_{4} g./ml.	1·13102	1·15343	1·17377	1·19953	1·21793	1·23946	1·25827	1·30381	1·33907	1·37081	1·40334
ϕ (apparent molal volume)	29·20	29·44	29·65	29·92	30·20	30·54	30·87	31·79	32·65	33·54	34·60

The partial molal volume $\bar{v}$ is calculated according to the method of Lewis and Randall; $\bar{v}=\phi+S/2{\cdot}303$ where S is the slope of the curve relating apparent molal volume to the number of moles of solute. The density of DNO_3 at 25° is 1·5228 g./ml.[20]

The molecular volume[20] of crystalline nitric acid is 33·1 ml. at −273°.[16] The apparent molecular volume[17] indicates existence of a trihydrate of NO_3^- and various hydrates of HNO_3,[18] and that at ordinary temperatures pure HNO_3 is 2·8–3·0% ionized.[19] The partial molal volume of DNO_3 is greater than that of HNO_3,[14] being 42·04 at 25° for DNO_3 but 41·932 for HNO_3.

Volume Changes on Hydration and Neutralization

With many acids and alcohols uniform decrease in contraction occurs on dilution with increasing amounts of water, but in the case of nitric acid[21] the curve of volume contraction as a function of the amount of water added passes through a maximum at approximately 0·2 moles H_2O per mole HNO_3. Thus addition of 1·80 g. of H_2O to 63·02 g. of pure HNO_3 gives rise at 20° to a volume contraction of 0·19 ml. as against 0·45 ml. when 95% HNO_3 is used. This has been explained in terms of disappearance of the bivalent cation $N(OH)_3^{++}$ and its replacement by the univalent ions $NO(OH)_2^+$, H_3O^+ and NO_3^-.

The volume changes that occur as nitric acid is neutralized by ammonia or sodium hydroxide show that the greatest volume change, which is about 0·6%, occurs at the point of neutral salt formation. This change is an expansion to a maximum when sodium hydroxide is added, but a contraction to a minimum with ammonia.[22]

Surface Properties and Diffusion

The surface tension[35] of nitric acid has been measured[23] by the maximum bubble pressure technique and is 41·15 dynes/cm. for the pure acid at 20°C. Measurement of relative surface tension based on a comparison of weights of drops formed at the end of a cylindrical tube show[24] that at 21° the surface tension of nitric acid decreased with increasing concentration following approximately the law $A - A' = A(1 - Kr) = A(1 - Kr_m)$ in which r is the concentration, r_m the molar concentration, and $K = 0{\cdot}00380$.

The adsorption isotherms of 0·001–0·003 N. HNO_3 solutions[25] have been found to form one of a family of similar curves obtained also with other acids. Data for the velocity of adsorption of nitric acid on copper[26, 27] show that the rate-determining step in the dissolution of copper in the acid is adsorption of HNO_3 molecules. Experiments with silica gel using commercial 70% HNO_3 show[28] that at 20–25°, 24 to 24·4 g. of the gel adsorb 13·8 to 16·5 g. of nitric acid and that reactivation is possible. With ground fused silica[29] adsorption energies range from approximately −2 kcal. to over −4 kcal. for the fixed layer of NO_3^- ions as the equivalent concentration varies from 2×10^{-5} to 2×10^{-3}, whilst the inter-layer transference energies range from −7 to over −8 kcal. The adsorption of nitric acid on wood and sugar charcoals has been investigated.[30, 31] In a study of the dynamics of adsorption of the vapour on charcoal[32] it has been found that the adsorptive capacity does not depend much on the concentration of nitric acid in the vapour. Adsorption on cellulose[33] shows the existence of a compound with up to 14·8% N. Adsorption on hide[34] shows the adsorption coefficient to be independent of the amount of hide or the swelling and indicates that the adsorption process consists in the formation of solvates of the acid molecules and ions of the collagen. Some studies in electro-endosmosis[36, 37] have been reported and measurements of electrokinetic potentials of nitric acid solutions have been made.

Determination[38] of the diffusion of aqueous solutions of nitric acid in the concentration range 2 N to 0·05 N at temperatures of 18–20° shows the diffusion coefficients, corrected to 20°, to be 2·150 for 2 N, 2·141 for 1·5 N, 2·164 for 1 N, 2·227 for 0·5 N, 2·246 for 0·1 N and 2·266 for 0·05 N solutions. The speed of diffusion increases with lower concentrations, but the increase is small because even a 2 N solution is 70% dissociated.

Viscosity

The viscosity–concentration curves for nitric acid show[39] a maximum at 27 mol.-% HNO_3 at 0°, the maximum being lowered and shifted towards higher concentrations by increasing the temperature. The plot of viscosity of aqueous nitric acid solutions at -17°[40] against concentration shows the maximum deviation from an ideal curve, drawn on the assumption that an ideal liquid mixture is formed, at a concentration corresponding to HNO_3,H_2O. Other viscosity measurements have been interpreted in terms of polymerization[44] and ionic-atmosphere theories.[42] At 0° in the system HNO_3–H_2O–NO_2, the viscosity curve exhibits a maximum near 45% NO_2, the viscosity decreasing up to 1% H_2O and then increasing.[10, 13, 47, 48] The initial decrease may be due to suppression of self-ionization of the nitric acid by the added water:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

or to the interaction of water with dinitrogen pentoxide, N_2O_5.

At 0° the addition of nitric acid to water first produces a decrease in the viscosity, and thereafter a rise to a maximum occurs at 63% of nitric acid. The initial drop is attributed to depolymerization of water. Increasing temperature decreases this 'negative viscosity' effect which can be explained as due to lowering of the degree of polymerization of water. The shift of the maximum of these curves with temperature has led to speculation on existence of a dihydrate.[47]

The variation of viscosity of nitric acid with concentration is set out in Table V.[41]

Table V.—Viscosity of Aqueous Nitric Acid at 25°

$\times 10^{-5}$ poise	914	951	991	1042	1120	1187	1327	1487	1758
Concentration (moles/l.)	0·987	2·010	2·810	3·744	4·863	5·667	7·257	8·900	11·92

The viscosity of red and white fuming nitric acid is given in Table VI.[43]

Table VI.—Viscosity in Centipoises of Fuming Nitric Acid (*at bubble point*)

Temperature °C.	Red[a]	White[b]
10	2·040	1·013
20	1·635	0·875
30	1·350	0·758
40	1·105	0·651
50	0·925	0·585
60	0·785	0·520
70	0·670	0·457
80	0·570	0·435
90	0·490	0·408
100	0·425	0·391
112	0·370	0·386
120	0·315	0·385

[a] Initial composition in parts by weight: 0·833 HNO_3, 0·143 NO_2, 0·024 H_2O.
[b] Initial composition in parts by weight: 0·942 HNO_3, 0·040 NO_2, 0·018 H_2O.

Other determinations of the viscosity of white fuming nitric acid have been made.[12, 44] At -20°C. it is 2 centipoises for the following mixture: 97·35% HNO_3, 1·57% NO_2, 1·08% H_2O.

The viscosity of nitric acid has also been deduced from the heat of vaporization,[51] using the formula:

$$\eta = \frac{hN}{V} \exp \frac{\Delta H_{\text{vap}} - RT}{CRT}$$

where η = viscosity in poises
h = Planck's constant
V = molar volume of liquid in ml. mole^{-1}.
C = 3·08
N = Avogadro's Number

The viscosity of nitric acid–sodium hydroxide mixtures reaches a minimum at the neutralisation point.[50]

Specific Heat

The specific heat C of nitric acid solutions at 20° over the range of 200–1650 moles of water, N, per mole of solute is stated[52] to be given by:

$$C = 0{\cdot}97203 + 0{\cdot}0000328N - 0{\cdot}000000010N^2 \pm 0{\cdot}0005$$

On the assumption that the vapour pressure and fugacity are equal, equations have been presented[53] for the heat capacities of liquid and gaseous nitric acid. The calculated values are: at 232–305°K. for the liquid $C_p = 28{\cdot}64 - 8{\cdot}0 \times 10^{-3}T$; at 275–500°K. for the gas $C_p = 6{\cdot}57 + 18{\cdot}75 \times 10^{-3}T$. These data were calculated from the results of Forsythe and Giauque[54] who showed that the heat capacity of solid nitric acid increases from 0·547 cal. degree^{-1} mole^{-1} at 13·51°K. to 16·436 at 225·42°K. (melting ensues at 231·51°K.) and decreases in the liquid from 26·73 at 238·57°K. to 26·32 cal. degree^{-1} mole^{-1} at 302·89°K. The heat capacity of the monohydrate HNO_3,H_2O increases from 0·610 at 14·91°K. to 21·55 at 227·53°K.; after melting at 235·48°K. it increases from 42·94 at 239·89°K. to 43·78 cal. degree^{-1} mole^{-1} at 298·63°K. For the trihydrate $HNO_3,3H_2O$ the heat capacity varies from 0·924 at 14·84°K. to 41·11 at 248·69°K.; after melting at 254·63°K. it increases from 74·43 at 254·85°K. to 77·71 cal. degree^{-1} mole^{-1} at 295·58°K.

The heats of dilution of an aqueous nitric acid solution corresponding to $HNO_3,10H_2O$ with increasing additions of water up to the composition HNO_3, $400H_2O$ have been determined and the specific heats of each solution have been calculated.[55] The data are compared with corresponding data obtained for aqueous solutions of alkali nitrates, chlorides and hydroxides.

Heat capacities for the ions of nitric acid at 25° are[56]: $C_p°\ H^+ = -31{\cdot}7$, $NO_3^- = +3{\cdot}8$ on a scale based on NH_4NO_3 and NH_4Cl. The partial molal heat capacity of nitric acid in water between 18°C. and 25°C. is calculated as $-21{\cdot}3$ cal. mole^{-1} degree^{-1}.[57]

The effect of dissolved NO_2 on the heat capacity is shown[58-9] in that a 40% HNO_3 solution has a specific heat of 0·669 compared with 0·402 for a mixture of 40% HNO_3, 58·5% H_2O, 1·5% NO_2. The specific heat of white fuming nitric acid is 0·4225 B.Th.U./lb. °F., from −40°C. to 70°C. rising to just over 0·435 at 150°C.[11, 12]

Velocity of Sound

The velocity of sound and compressibilities for two samples of white fuming nitric acid are given[11] in Table VII.

Table VII.—Compressibility of White Fuming Nitric Acid

Composition: HNO_3	97·08	97·52
NO_2	0·22	0·28
H_2O	1·91	2·11
$Fe(NO_3)_3$	0·79	0·09
d at 25°C.	1·494	1·497
Velocity of sound, m./sec. at 25°	1239·2	1239·7
Adiabatic compressibility β_a	42·74	42·61
Isothermal compressibility β_t	55·99	53·75
Ratio of specific heats = β_t/β_a	1·31	1·26

Freezing Point

The freezing point of pure nitric acid is −41·62±0·05°.[60] Freezing point determinations have been used to determine activity coefficients.[61–2] The freezing points of aqueous solutions vary from 0·1007° for 0·02833 moles/1000 g. H_2O to 34·009° for 6·615 moles/1000 g. H_2O. The activity coefficients are calculated at 0°C. to be 0·9660 for 0·001 g. HNO_3/1000 g. H_2O and 0·8816 for 3 g./1000 g. H_2O. Other claims are[63] that the activity coefficient at 0·002m. is 0·9534, at 3m. 0·8449, and at 4m. 0·9587, these values being calculated from the freezing points which vary from 0·0073° at 0·002m. to 17·77° at 4m. (m. = molality).

The effect of N_2O_5 on the freezing point of nitric acid[64–6] has been interpreted as indicating the dissociation of nitric acid to be: $3HNO_3 = NO_2^+ + NO_3^- + HNO_3,H_2O$ with a heat of dissociation of approximately 10 kcal. Cryoscopic determinations of nitrates in nitric acid indicate no association.[67] A eutectic at −73° in the HNO_3–N_2O_4 system[3, 68] occurs at 18% N_2O_4. A compound $2HNO_3,N_2O_4$ may exist.[68]

Freezing-point determinations on solutions of selected solutes in 100% nitric acid show that the acid contains about 8 mol.-% of dissociation products, including N_2O_5, NO_3^-, NO_2^+, H_3O^+, and possibly $H_2NO_3^+$.[60] Other work shows the presence of the hydrates HNO_3,H_2O[205] and $HNO_3,3H_2O$.[199, 209]

Vapour Pressure

Early measurements of the total and partial vapour pressures of nitric acid[67] show that for 20·65% HNO_3 at 50°C. the total vapour pressure is 79·9 mm., the partial pressure of HNO_3 being zero. For the 68·42% acid at the same temperature the total vapour pressure is 35·7 mm., the partial pressure of nitric acid being 13·7 mm. For 80·23% acid at 52°C., the total pressure is 50·3 mm. and the partial nitric acid pressure 35·2 mm. For 90·63% acid, the corresponding figures are 136·2 mm. and 123·6 mm.

Several later measurements have been carried out[19, 69, 70, 74–76] and the vapour pressure of 100% HNO_3 has been given as 14·7 mm. at 0°C. and 48·0 mm. at 20°C. For 50% acid, the nitric acid and water vapour pressures are 0·095 and 1·97 mm. at 0° and 0·49 and 7·53 mm. at 20°.[76] At 50°C. 20% HNO_3 gives 77 mm. water vapour and negligible nitric acid partial pressures, 80% HNO_3 gives 14 mm. water vapour and 32 mm. nitric acid partial pressures.[69] The heat of vaporization is 9415 to 9436 cal./mole for 99·91% HNO_3 at 20°C. There is apparently a positive deviation from Raoult's Law over the range 90 to 100 mol.-% HNO_3.[83] Vapour pressure data calculated from Forsythe and Giauque's work[53, 54] are in good agreement with experimental data and a boiling point of 84° is indicated. The free energy of vaporization is given by:

$$\Delta F^\circ = 14{,}744 + 22{\cdot}07T \ln T - 13{\cdot}38 \times 10^{-3}T^2 - 166{\cdot}26T$$

At 12·50° 4·8 N. solutions of HNO_3 and HCl have the same vapour pressure, $2{\cdot}10 \times 10^{-2}$ mm.[71] Vapour pressure measurements of 14 N. HNO_3 solution indicate the presence of a dihydrate. A monohydrate is indicated in vapour pressure work on 75–100% HNO_3[73] and a hemihydrate, $(HNO_3)_2,H_2O$ above 90% HNO_3.[83] Comparison of known data with the Duhem equation[54, 72]:

$$\mathrm{d}\log p_{HNO_3} = -(N_{H_2O}/N_{HNO_3})\,\mathrm{d}\log p_{H_2O}$$

has given very divergent interpretations of structure. An attempt has been made[77] to correlate partial vapour pressure data and molecular composition with the conclusion that the maximum number of H_2O molecules that can form bonds with one molecule of HNO_3 is 15. Continuation of this work[78] showed the presence of $2HNO_3,3H_2O$ formed by hydrogen bonding. Work on the NO_2–HNO_3 system[82, 84–5] shows that Henry's Law does not apply to the partial pressure of the NO_2[79] and indicates that the equilibrium $HNO_3{\cdot}NO_2 + H_2O \rightleftharpoons HNO_3,H_2O + NO_2$ exists. N_2O_5–HNO_3 mixtures have vapour pressure curves that follow the sum of component vapour pressures[80] and are similar to HNO_3–H_2O vapour pressure curves.[81]

A maximum occurs near 85·7% N_2O_5 and a minimum at 87·5% N_2O_5. The equation $\log P_a = A \log P_w + B$ has been deduced[51] where P_a is the total vapour pressure, P_w the vapour pressure of water at the same temperature and

$A = 0{\cdot}827$, $B = 1{\cdot}2877$ for the composition: 0·7537 HNO_3, 0·1928 NO_2, 0·0535 H_2O
$A = 0{\cdot}944$, $B = 0{\cdot}5930$ for the composition: 0·8596 HNO_3, 0·0202 NO_2, 0·1202 H_2O

Measurements of the vapour pressure of the nitric acid–sulphuric acid system[86, 88] indicate that addition of water to a mixture of these two acids decreases the total vapour pressure at first to a minimum at the composition corresponding to $(HNO_3)_6,N_2O_5$; further addition of water converts the N_2O_5 to HNO_3. Work on the phosphoric acid–nitric acid system[86, 87] shows that, because phosphoric acid has little tendency to form hydrates, the vapour pressure curve is simply a function of the nitric acid content.

Boiling point

The boiling point of aqueous nitric acid is given in Table VIII[90–92]:

Table VIII.—Boiling Point of Aqueous Nitric Acid (760 *mm.*)

w/w% HNO_3	0	6·1	12·9	17·0	20·3	23·3	24	27·2
B. pt. °C.	100·0	100·6	102·1	103·3	104·2	105·2	105·6	106·6

w/w% HNO_3	31·0	32·7	34·5	37·9	41·0	43·0	47·3	49·7
B. pt. °C.	107·9	108·7	109·2	110·5	111·7	112·5	114·1	115·2

w/w% HNO_3	52·0	53·6	56·0	58·5	62·0	67·5	69·2	71·7
B. pt. °C.	116·0	117·0	117·7	118·9	119·6	120·6	120·4	120·0

w/w% HNO_3	72·2	73·7	75·3	77·4	82·1	85·6	89·6
B. pt. °C.	119·7	118·9	117·6	114·4	110·1	106·6	101·5

The last four determinations involved decomposition on boiling. The decomposition of concentrated nitric acid increases with prolonged boiling[89] while the temperature falls.

Heats of Formation, Hydration and Dissociation, Free Energy and Entropy

Forsythe and Giauque[54] found the heat of infinite dilution to be −7971, −4732 and −2123 cal./mole for HNO_3, HNO_3–H_2O and HNO_3–$3H_2O$ respectively, with the corresponding entropies as 371·9, 51·84 and 82·93 cal./degree/mole. Having found no appreciable association in the vapour these entropies were used with the entropy of water and heats of hydration to calculate the free energy of hydration. It was found that for:

$$HNO_3\ (l) + H_2O\ (l) = HNO_3,H_2O\ (l)$$
$$\Delta F_{343{\cdot}1^\circ K} = -2523 \text{ cal. (Third Law) or } -2495 \text{ cal. (isothermal)}$$

and that for:

$$HNO_3\ (l) + 3H_2O\ (l) = HNO_3,3H_2O\ (l)$$
$$\Delta F_{323{\cdot}1^\circ K} = -4404 \text{ g.-cal. (Third Law) or } -4406 \text{ g-.cal. (isothermal)}$$

This agreement was held to indicate that the integral $\int_0^T C_p \, d \ln T$ gives the correct entropies for HNO_3 and its hydrates, and that if hydrogen bonding occurs in the lattice structure of these solids, no randomness occurs at low temperatures.

The equilibrium constant for the reaction

$$NO_2OH{,}H_2O + 4H_2O \rightleftharpoons NO_3^- + H^+(5H_2O)$$

is 1·2 at 30–35°C.[179]

The entropy of HNO_3(g) is 63·62 g.-cal./degree/mole at 298·1°K. and 1 atmosphere. This value, used to determine the internal rotation of the HNO_3 molecule, shows a double rotational barrier of 7000 g.-cal./mole. The partition function gives $S^\circ_{298\cdot1} =$ 63·67.[107] Other work[84, 111] shows the OH rotation barrier to be 9–10 kcal./mole.

Statistical-mechanical calculations based on Raman spectra give the thermodynamic data at 298·16° in Table IX.[112]

Table IX.—Thermodynamic Data for Nitric Acid and Deuteronitric Acid

	$-(F^\circ - H_0^\circ)/T$		$(H^\circ - H_0^\circ)/T$		S°		C_p°	
	A	B	A	B	A	B	A	B
HNO_3	53·99	54·22	8·92	9·46	62·90	63·68	11·42	12·80
DNO_3	54·17	54·57	9·03	9·79	63·20	64·36	11·77	13·39

(A gives the contributions of translations, overall rotations and vibrations, while B includes internal rotation.)

The data of Forsythe and Giauque[54] have been used to calculate the free energy of formation of nitric acid from its elements.[102] The results at 298·16° were:

$$HNO_3\ (l),\ \Delta F^\circ = -19{,}032 \text{ g.-cal./mole}$$
$$HNO_3\ (g),\ \Delta F^\circ = -17{,}556 \text{ g.-cal./mole}$$

Calorimetric and spectroscopic evidence[98] give the following valence change energies:

$$N^0 \rightarrow N^{I} = 9\cdot2 \text{ kcal.},\quad N^0 \rightarrow N^{II} = 106\cdot9 \text{ kcal.}$$

Work on the decomposition of nitric acid has shown the energy of activation for the decomposition reaction to be about 5 kcal at below 400° in a heterogeneous reaction, 21·0–23·2 kcal. in the liquid phase and 35·5 kcal. in the gas phase.[93] The reaction between HNO_3 and NO, possibly a part of the decomposition reaction at low temperatures, has an activation energy of 13 kcal./mole.[99]

The reaction $HNO_3 \rightarrow H^+ + NO_3^-$ is said to have a standard free energy of dissociation (ΔG°) of −1·0 kcal. at 25°C.[95] For the reaction $4HNO_3$ (g) $\rightleftharpoons 4NO_2 + O_2 + 2H_2O$, $\Delta G^\circ_{298} = 11\cdot5$ kcal., and the value of

$$K_p = P_{NO_2}P_{O_2}P^2_{H_2O}/P^4_{HNO_3}$$

is $1\cdot86 \times 10^{-10}$ atm.[3] at 12·5°C.[96] The heat of dissociation for the reaction: $3HNO_3 = NO_2^+ + NO_3^- + H_2O{,}HNO_3$ is about 10 kcal.[64, 94, 96]

The partial molar free energy of nitric acid in solution is 6·798 kcal. at 0·002 M. and 1·365 kcal. at 4·0 M.[63] The heat of dilution follows Debye's laws only at low concentrations.[103] One mole of H_2O added to 120 moles of HNO_3 yields 4050 cal. with 97–97·5 wt.-% of HNO_3[104]; this figures drops to 450 cal at 86·51 wt.-% of N_2O_5. The heat of dilution over the range $HNO_3{,}4\cdot5H_2O$ to $HNO_3{,}3800H_2O$ is constant at 14·85 kcal./mole HNO_3.[105] The differential heat of solution at infinite dilution has been calculated to be 7970 g.-cal./mole.[106] The entropy change at 25° on mixing nitric acid with water is a minimum at 40% HNO_3.[106] The standard entropies of formation of the hydrates of HNO_3 are 4·2 g.-cal./mole/degree for the monohydrate and 10·7 for the trihydrate.[61, 100, 113]

Heat of Neutralization[66, 108–110]

The heat of neutralization with ammonia is 20·89 kcal.[97] The heat of neutralization at 20° with potassium hydroxide and sodium hydroxide is given in Table X.

Table X.—Heat of Neutralization of Nitric Acid

Mols. H_2O in reactants	50	100	200	800	00
Mols. H_2O in products	51	101	201	801	1
With potassium hydroxide (g.-cal.)	14724	14325	14086	13834	13700
With sodium hydroxide (g.-cal.)	14012	13892	13837	13756	13705

Optical Properties

The magnetic rotation of plane-polarized ultra-violet light (3441–3632 A.) shows[115] that, while the specific rotation for most electrolytes is nearly independent of the concentration or decreases with increasing concentration, the value for nitric acid increases. The molar rotation decreases to less than one-third on dissociation.[160]

REFRACTIVE INDEX

At 25° and 5461 A.[119] for dilute HNO_3 up to 10 N., the plot of $\Delta n/\Delta c$ against c (n = refractive index, c = molarity) shows an abrupt change at 3·35 N. The molar refraction R undergoes a sudden change at 7 N. Between 3·5 N. and 6 N. $\Delta R/\Delta c$ is constant as it is between 7 N. and 10 N., thus indicating that n and R are independent of the degree of dissociation but are dependent on the structure. A break in the molar extinction curve at 10 N. with a minimum at 23·6 N. has been attributed to the presence of N_2O_5.[135] Changes in the refractive index at high concentrations have been attributed to a change from nitronium nitrate $[NO(OH)_2][NO_3]$ to the pseudo acid $NO_2.OH$.[118]

The refractive index of deuterium nitrate solutions is given in Table XI.[14]

$$R_L = \frac{M}{d}\left\{\frac{n^2-1}{n^2+2}\cdot\frac{100}{dp} - \frac{n_0{}^2-1}{n_0{}^2+2}\cdot\frac{100-p}{d_0 p}\right\}$$

R_L = molar refraction
n = refractive index of the solution
n_0 = refractive index of the solvent
d = density of the solution
d_0 = density of the solvent
M = mol. wt. of the solute
p = concentration in g./100 g. of solution

Table XI.—Refractive Index of Aqueous Deuterium Nitrate[221]

Concentration (g./100 g. water)	4·606	8·507	11·971	16·263	19·34	22·91	26·05	33·76	40·02	46·02	52·76
n_D^{20}	1·33485	1·34047	1·34550	1·35180	1·35623	1·36121	1·36549	1·37518	1·38172	1·38724	1·39214
R_L	10·439	10·424	10·401	10·376	10·361	10·327	10·303	10·230	10·154	10·108	10·063

ABSORPTION SPECTRA

The absorption at 425 mμ of NO_2–HNO_3 mixtures indicates[122] that at $<1\%$ of NO_2 the nitrogen dioxide is 70% ionized to NO^+ whereas the nitric acid is only 5% ionized to NO_2^+ ions.[114, 116, 117, 120, 124–126, 162, 163, 198]

Nitric acid exhibits weak, long-wave, light absorption together with strong absorption at a shorter wave-length.[137] The first is said to represent transition to an excited state and the second photochemical decomposition.

Comparison of the absorption spectra for nitric acid and potassium nitrate indicates[127] presence of a true acid having the form $(NO_3)H$ or $(NO_3).H_3O$, while comparison of the spectra of ether solutions of the acid and of esters, NO_2OR, suggests the pseudo acid form NO_2OH in such media. In ether and in acetic acid, nitric acid may be present as 60% associated ions[128] and the remainder as undissociated molecules. Absorption of absolute ethereal solutions is continuous, but not if any water is present.[129]

All cations appear to influence the absorption of the nitrate ion,[128] but if the cation is not easily deformed, its influence is less. The spectra of HNO_3–H_2SO_4 mixtures indicate the presence of N_2O_5.

Ultra-violet Spectra. Several references to the interpretations of the structure of nitric acid[198, 217–219] are referred to later (p. 308).

RAMAN SPECTRA

The Raman lines for nitric acid and deuterium nitrate are given in Table XII: (cm.$^{-1}$)

Table XII.—Raman Spectra of Nitric Acid and Deuterium Nitrate

HNO_3	3386	1680	1538	1394	1301	1049	926	675	607	480	
DNO_3	2476	1336	1645	1534	1393·5	1305	1036	924	672·5	570·5	370

Early measurements[130] have shown the following principal groups of radiation in the Raman effect with nitric acid solutions over the concentration range 2·7 to 13·4 moles/litre: (i) 720, 1049 and 1400 cm.$^{-1}$, peculiar to the NO_3 group; (ii) 640, 690 and 950 cm.$^{-1}$, which disappear at concentrations of the order of 10 moles/litre; (iii) the band 1306 cm.$^{-1}$. This last band does not appear at concentrations lower than 7 moles/litre and is supposed to be due to presence of NO_2 groups. This conclusion is based on the results of observations of dilute and saturated solutions of nitrites at frequencies of 815, 1291, 1326 cm.$^{-1}$, and comparison with results obtained by other investigators for organo-nitro compounds which show that wherever the NO_2 group exists, the frequency is close to 1300 cm.$^{-1}$. This frequency indicates that the molecular form NO_2OH exists in concentrated nitric acid. Ingold and Millen[222] pay particular attention to a line at 1535 cm.$^{-1}$ which they assign as the first over-tone of the out-of-plane vibration of the NO_3 group. The nitrate ion frequencies are given as 720, 1050 and 1360 cm.$^{-1}$, the nitronium ion frequency as 1400 cm.$^{-1}$. Other lines are also assigned.

A line at 480 cm.$^{-1}$ in anhydrous HNO_3 may be the frequency of restricted internal rotation of the H atom.[221] Studies of the 100% nitric acid and its monohydrate[136] show that the 100% acid forms NO_2OH and partly decomposes to the anhydride N_2O_5. The nitric acid molecule is said to have at most a twofold symmetry axis. The spectrum of the monohydrate resembles that of anhydrous nitric acid so closely that the existence of an orthonitric acid in the liquid state can be excluded. In the crystalline state the spectra of the acid and its monohydrate are also very similar, but of a quite different type from that of the liquid state. The transformation of pseudo forms, NO_2OH and NO_2OH,H_2O into $H(NO_3)$ and $(H_3O)(NO_3)$ with the transition from liquid to solid is probable, but it is thought that orthonitric acid does not exist in the solid state.

The effect of temperature on Raman lines of nitric acid and its ions shows[138, 139] that dissociation decreases with increasing temperature and that in the dissociation to NO_3 ions the rate of decrease of dissociation with temperature is less in dilute solutions. The thermodynamic ionization constant determined from Raman spectra is 21.[140] An earlier value, believed to be less reliable, is 24[133]; this agrees well with estimates based on light-absorption measurements.[134] See also[180].

Certain thermodynamic functions of nitric acid have been deduced from Raman spectra[112]; some of these are given on p. 303.

INFRA-RED SPECTRA

Comparison of the infra-red spectrum of nitric acid with that of water shows for concentrated solutions[132] a similar absorption to that of water at higher temperatures: the acid sharpens the 0·77 μ band of water. The spectrum of the liquid monohydrate has been stated[215] to be the same as that of HNO_3, but below 2000 cm.$^{-1}$ the spectrum of the crystalline monohydrate is different. The 738, 815, 1381 cm.$^{-1}$ bands are attributed to the NO_3^- ion. The 750 cm.$^{-1}$ frequency is discussed by Redlich [214] together with the frequencies in the 771–791 cm.$^{-1}$ range found in the vapour. Measurements of infra-red spectra in various solvents have been carried out.[216]

The vibration and rotation bands have been determined[107] and they show that the frequency of deformation out of the plane of the NO_3^- ion to be 762 cm^{-1}. The spectra of HNO_3 and DNO_3 vapours[84, 111, 121] show a barrier of rotation for $-OH$ or $-OD$ of about 10 kcal./mole. This is probably large because of internal hydrogen bonding. The wave-lengths given are: (cm.$^{-1}$)[84]

HNO_3 (vapour)	3560	3390	3000	2627	2585	1710	1335	1320	1206	886	765	583	465
DNO_3 (vapour)	2980	2627	1685	1313	1114	1014	888	764	543				

and assignation to various stretching and bending frequencies etc. is given.

Thermal Properties

The thermal diffusion constant of nitric acid and other compounds has produced the following order[142, 143]:

$$NaOH > HCl,\ H_2SO_4,\ HNO_3 > CuSO_4,\ Na_2SO_4,\ Na_2CO_3$$

The thermal conductivity of white fuming nitric acid is 0·15 B.Th.U./hr, sq. ft., °F./ft. at 0° F., and increases linearly to 0·165 at 85° F.[12]

Electrical Properties

The limiting cathode current density–concentration curves for nitric acid are smooth[144, 145] at 25°, 60° and 90°; the current is appreciable in a 2·5 M. solution at 50° and in a 5 M. solution at 25°. At higher concentrations and temperatures deviations from the curve begin, and there are differences between values obtained with a rising current and those obtained with a falling current. This is explained in terms of dehydration of hydrated HNO_3 molecules, or depolarization by H^+ ions.

The cathode potential becomes more electropositive at higher concentrations, with a sharp rise at 3·5M. when non-ionized HNO_3 is said to appear.[146] The main electron acceptor at the cathode seems to be NO_2^+ ions.

A study of the HNO_3–HNO_2 reduction potential from measurements of the e.m.f. of the cell $Pt|HNO_3,HNO_2$ soln.|satd. $KNO_3|$N.$KCl–Hg_2Cl_2|Hg$ shows that within the range for $\log C_{HNO_2} = \bar{3}{\cdot}5$ to $\bar{1}{\cdot}0$ a relation exists: $e = e_0' - 0{\cdot}0296 \log C_{HNO_2}$ for each concentration of HNO_3.[148] The cathodic behaviour of $HNO_3|HNO_2$ solutions indicated[147] that the potential is governed by such reactions as:

$H^+ + NO_3^- \rightleftharpoons HNO_3$ (fast); $HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O$ (velocity determining); $N_2O_4 \rightleftharpoons 2NO_2$ (fast); $2NO_2 + 2e \rightarrow 2NO_2^-$ (velocity determining); $2NO_2^- + 2H^+ \rightleftharpoons 2HNO_2$ (fast).

Tafel's equation, for oxygen overvoltage, $\eta = 1{\cdot}102 + 0{\cdot}114 \log i$, is valid for current densities 10^{-7} to 10^{-1} amp./sq. cm.[149] in dilute HNO_3, but not for the concentrated acid.

An investigation of hydroquinone–quinhydrone potentials in the cell: Pt|quinone hydroquinone (15°)|HNO_3|quinone hydroquinone|Pt (35°), shows that the cold electrode is positive[151]; the e.m.f. is initially 0·44 volt for 0·1 M. HNO_3. The Soret coefficient, which is a measure of the relative concentration change in a temperature gradient, for nitric acid[150, 151] is 103×10^{-4}.

The electrocapillary curves for nitric acid in various organic solvents show[152] that in the systems M$\underset{\pi_1}{|}$Phase I$\underset{\pi_3}{|}$Phase II$\underset{\pi_2}{|}$M the absolute potentials π_1, π_2 are equal. The phases are formed by shaking aqueous nitric acid with an organic solvent until distribution equilibrium is attained.

The dipole moment for the NO_3 group is 2·73.[153]

At low concentrations the dielectric constant of nitric acid aqueous solutions decreases with increasing concentration and at high concentrations it increases.[155–7]

The resonance curves for nitric acid solutions are similar to those for hydrochloric and sulphuric acids.[154]

CONDUCTIVITY

The conductivity of nitric acid is less than those for hydrochloric, sulphuric and perchloric acids.[170] The high conductivity of pure nitric acid may be due to the structure $[NO(OH)_2].NO_3$ or $[N(OH)_3][NO_3]_2$.[127] Early measurements give the equivalent conductivity of nitric acid as 385·0 and suggest complete dissociation.[168, 45] The conductivity curve shows a maximum at 11 mol.-% with a break at 25 mol.-% which is quite sharp at 0°C. but less so at 30°. These data have been held to indicate the existence of the trihydrate.[172]

The molar conductivity of concentrated nitric acid is proportional to the cube root of the concentration.[169] NO_2–HNO_3 mixtures exhibit a negative temperature coefficient for specific conductivity in some cases, and a minimum occurs at 96 w/w% HNO_3.[48] The addition of small amounts of NO_2 to HNO_3 results in a significant increase in conductivity[46] with a maximum of 58·3 $(\text{ohm-cm})^{-1} \times 10^2$ at 0·3 wt. fraction of HNO_3 and a minimum of 1·31 $(\text{ohm-cm})^{-1} \times 10^2$ at 0·97 wt. fraction. The addition of water causes a decrease, then an increase, and finally a decrease. In the N_2O_5–HNO_3 system, the specific conductivity rises at 25°C. to a maximum of $86{\cdot}22 \times 10^2$ at 5·786 mol.-% N_2O_5, and a minimum of $1{\cdot}386 \times 10^2$ at 45·70% N_2O_5.[48]

Measurements of the cation transport numbers in nitric acid[174] agree with a theoretical limiting value. The H^+ mobility is the same as in hydrochloric acid up to 0·2 moles/litre, but NO_3^- mobilities may be higher than in aqueous KNO_3 or $AgNO_3$. If u is the anion mobility and v the cation mobility then $u\mathrm{d}v/\mathrm{d}t - v\mathrm{d}u/\mathrm{d}t = -98$ for HNO_3.[175] The transport number of the nitrate ion in HNO_3 is 0·1559.[168]

Other conductivity determinations show that (i) the dissociation constant for nitric acid in pyridine is $4{\cdot}96 \times 10^5$,[175] (ii) the conductivity in H_2O is 1·3885 times that in D_2O, (iii) the conductivity at infinite dilution in D_2O is 271·4 for DNO_3,[176] (iv) there is no combination with H_2SO_4 in mixtures.[151, 171, 173, 177–8]

MAGNETIC PROPERTIES

The gram-ionic susceptibility for the NO_3^- ion is $-20{\cdot}83 \times 10^{-6}$.[158] The molar susceptibility of solutions of nitric acid gradually increases with the concentration. At infinite dilution $\chi_m = 16{\cdot}6 \times 10^{-6}$.[159] The susceptibility for nitric acid and nitrogen pentoxide is given as 0·316,[161] and for NO_2^+ 0·424. The effect of a magnetic field on the conductivity has been investigated.[167]

The ^{14}N shifts in HNO_3 and $NaNO_3$ do not coincide.[164] $\Delta H/H(\times 10^{-4}) = 0{\cdot}52$ for 100% HNO_3, 0·00 for NO_3^- in $NaNO_3$ or NH_4NO_3. This shift is concentration dependent. The position of proton magnetic resonance is concentration dependent[165] and indicates that the dissociation constant for nitric acid is 22.[166]

Constitution and Structure of Nitric Acid

In view of the relatively complex constitution of nitric acid and its aqueous solutions, it is appropriate to gather together some of the information on this subject; this is done in the following section, within which there is some duplication of information already given in the earlier main sections of this account. For some relevant general reviews, see references.[187, 188]

Investigations into dissociation, conductance etc. of nitric acid have revealed[189] that nitric acid solutions consist of α HNO_3, β (H^+nH_2O,NO_3^-), γ_1 HNO_3,H_2O, γ_3 $HNO_3,3H_2O$ and δ H_2O together with a hemihydrate, $(HNO_3)_2,H_2O$ where the concentration exceeds 70% HNO_3. Values of α, β, γ_1, γ_3 and δ vary with the concentration. Other electrolytic data[168] indicate that nitric acid is completely dissociated. There is a minimum in the specific conductivity[48] at 96 w/w% HNO_3. The conductivity–concentration curve shows the presence of $HNO_3,3H_2O$.[46]

Vapour pressure data indicate[71] presence of only one hydrate, $HNO_3,2H_2O$, in 14 N. solution. The usual volume changes on dilution[21] do not occur at above 95 w/w% HNO_3, possibly owing to the disappearance of bivalent cations like $N(OH)_3^{++}$ at this concentration in favour of NO_2^+,H_2O. The heat of dilution passes through a maximum at 97% HNO_3[193] and N_2O_5 and $NO_3^-,nHNO_3$ are said to be present.[104]

Deviations from specific gravity additivity[190] have been used to prove the existence of a hydrate $HNO_3,3H_2O$, other hydrates and the hydrated NO_3^- ion.[17–18] HNO_3, $3H_2O$ is present at temperatures between 5° and 30°.[190] Pure nitric acid is 2·8–3·0% ionized[19] and in concentrations above 90 mol.-% $(HNO_3)_2,H_2O$ is formed. The volumes of the NO_3^- ion as given by viscosity and density data and the size of this ion in crystals are approximately equal; it is therefore suggested that the NO_3^- ion may not be hydrated.[41] Further measurements of volume changes on dilution of nitric acid indicate[192] that $N(OH)_3^{++}$ is first formed followed in more dilute solutions by the ion $NO_3H_2^+$. The existence of the hydrate, $2HNO_3,3H_2O$ was confirmed[78] by measurements of the heat of vaporization, the molecules being held together by hydrogen bonds. On diluting the pure acid to 75% concentration, the principal reaction is the formation of a monohydrate[73] and a review of the evidence indicates existence of liquid hydrates with $\frac{1}{2}$, 1, $1\frac{1}{2}$, 3, 6 and 15 mols. H_2O per mol. HNO_3.[194] Thermodynamic properties of HNO_3,H_2O and $HNO_3,3H_2O$ are given by Forsythe and Giauque[54] and by Chedin[195]; the former authors conclude that no appreciable association exists in the vapour over nitric acid solutions. Electron-diffraction photographs of the vapour indicate that the NO_2 group has the same planar structure in the vapour as gaseous NO_2.[162]

Calorimetric and spectrographic data associated with valency changes of nitrogen have shown that the nitrogen atom in nitric acid is quinquevalent.[98]

Ultra-violet spectra indicate the presence of some N_2O_5 at high concentrations[217] and HNO_3 at low concentrations.[218] Raman spectra determinations provide evidence of the existence of N_2O_5 in solutions stronger than 97% HNO_3[136] which also contain NO_2OH molecules with a two-fold symmetry axis.[128, 130, 131, 137] The breadth of the 3400 cm.$^{-1}$ Raman line is interpreted[222] as arising out of intermolecular hydrogen bonding, the 3400 cm.$^{-1}$ line being an –OH stretching line. The ionic character of the –OH bond in nitric acid is shown by the weak hydrogen bonding frequency in the Raman spectra.[222] The two frequencies at 1400 cm.$^{-1}$ and 1050 cm.$^{-1}$ are interpreted as due to the presence of the nitrate and nitronium ions which can occur by the self-ionization of nitric acid ($\sim$ 3%). The addition of water suppresses the self-ionization spectra, changes the forms of hydrogen bonding, and forms the nitrate ion. The infra-red spectrum of HNO_3,H_2O has been discussed.[215] Undissociated

HNO_3 is said to have a plane symmetry, C_{2v}.[196] In solutions about 10 N. ion-pairs of complex ions may be present.[129] The presence of the OH group in 100% HNO_3 has been shown.[220] The bond forces have been measured,[197] that for N=O being $11{\cdot}6 \pm 0{\cdot}2 \times 10^5$ dynes/cm. The presence of NO_2, NO_2^+ and NO_3^- is indicated.[107, 130, 198, 215, 219]

Viscosity measurements of aqueous solutions show the presence of $HNO_3,3H_2O$[39] which is stated to melt at $-37°$; the compound HNO_3,H_2O but no trihydrate could be found at $-17°$,[40] whilst at above 0° viscosity data did not support the existence of any hydrate.[47]

Magnetic susceptibility determinations for aqueous nitric acid indicate the presence of 50, 6, 4 and 2·5 moles H_2O per mole HNO_3,[159] whilst data for the Faraday effect show the probable presence of covalent linkages in the pure acid.[124] Proton magnetic resonance shift reflects association of HNO_3 molecules in solutions containing more than 50 mol.-% of the acid.[166, 167]

Electron diffraction measurements indicate[162, 221] a symmetry of C_s, the molecule being mostly in a plane. The N=O distance is 1·22A., N–O (hydroxyl) 1·41A.; angle O=N=O 130°, angle O=N–O 115°.

Electron density curves of $HNO_3,3H_2O$ have been obtained[162, 200]; the most likely structure of NO_3^- in solution is said to be a plane triangle with N–O distance of 1·2 A. (which agrees with the value 1·21 A. observed in the NO_2^- ion in crystalline nitrates).[202] In crystalline form HNO_3 and its mono- or trihydrates have been found[201] by *X*-rays to be orthorhombic. $HNO_3,3H_2O$ belongs to the space group $P2_12_12_1 - D_2^4$.[304, 206] $4HNO_3,H_2O$ has also been found in the solid state[205] at temperatures from $-57{\cdot}4°$ to $-59°$. In solution, the O atoms in the NO_3^- ion may be bonded to two H_2O molecules by hydrogen bonds,[202] the angle between the two H bonds being about 120°, and the length of the bond about 2·9 A.[202] or 2·49–2·82 A.[204] See also [203]. It is also stated[204] that there are 7 H bonds, one for each H atom in the unit cell.

Crystals of $HNO_3,3H_2O$ melt at $-18{\cdot}5°$.[206] HNO_3,H_2O has a space group $Pna2_1 - C_{2v}^9$ and crystallizes at $-37{\cdot}7°$.[207, 210–2] The O–N–O angle is 127°, N–O bond length 1·29 A. and O–N–OH angle 116·5°. The unit cell contains 4 molecules of HNO_3,H_2O. All the O and H atoms are involved in hydrogen bond formation. The anhydrous acid crystallizes in the monoclinic system[208, 212] with space group $P2_1/c - C_{2h}^5$ and with 16 HNO_3 molecules in the cell. The O–N–O angle is 134°, N–O bond length 1·24 A. O–N–OH angle 114°, the N–O–H angle $134 \pm 3{\cdot}5°$, the N–OH bond length $1{\cdot}30 \pm 0{\cdot}045$ A.[101] HNO_3 vapour has an O–N–O angle of $130 \pm 2°$ and N–O length is $1{\cdot}21 \pm 0{\cdot}02$ A. and $1{\cdot}41 \pm 0{\cdot}02$ A.[214]

The rate of dissolution of copper in nitric acid has been used to ascertain the presence of a hydrogen bridge between HNO_3 and H_2O molecules[184] in the liquid. Data for the concentrations of undissociated HNO_3 molecules in nitric acid solutions have also been obtained from measurements of the rate of dissolution of copper in the acid.[27, 184, 185] The solubility isotherms of the system CrO_3–HNO_3–H_2O indicate the presence of HNO_3,H_2O and possibly $2HNO_3,H_2O$.[141]

Measurements of the exchange of the oxygen isotope ^{18}O between nitric acid and water indicate the presence in the solution of the species $H_2NO_2^+$, NO_2^-, N_2O_3, NO^+ and NO_3^-.[181–183]

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SECTION XXXI

CHEMICAL PROPERTIES OF NITRIC ACID

BY M. G. B. WRIGHT AND P. EVANS

OXIDATION—REDUCTION REACTIONS

Nitric acid is reduced by hydrogen in the presence of an active platinum catalyst to produce ammonia and nitrous acid, the more nitrous acid being produced the more concentrated is the nitric acid.[1] The reactions of nitric acid with metals are given later in this section.

Nitric Oxide

Nitric acid reacts with nitric oxide to form nitrous acid according to the overall equation:

$$HNO_3 + 2NO + H_2O \rightarrow 3HNO_2$$

The rate is proportional to the first power of each of the concentrations of hydrogen ion, nitrate ion and nitrous acid, nitrous acid being an autocatalyst for the reaction. The rate is independent of the partial pressure of nitric oxide and decreases slightly with increasing ionic concentration. Sulphate ions retard the reaction which occurs in two steps:

$$(1) \qquad H^+ + NO_3^- + HNO_2 \rightarrow N_2O_4 + H_2O$$

$$(2) \qquad N_2O_4 + 2NO + 2H_2O \rightarrow 4HNO_2$$

The first step is rate-determining.[2]

The velocity of absorption of nitric oxide gas by nitric acid solution increases with temperature and also with the addition of hydrochloric acid[3, 4]; low concentrations, 10^{-8}–10^{-9} N., of silver or mercuric ions also accelerate the absorption, but higher concentrations of these ions retard the absorption.[5] The rate of reduction of nitric acid increases approximately proportionally to the rate of passage of nitric oxide through it. The heterogeneous nature of the reaction manifests itself by a decrease in reaction rate with increasing reaction volume or decrease in the surface area exposed to the gas.[6]

The kinetics of the gas phase oxidation of nitric oxide with nitric acid vapour are complex, with surface effects very prominent.[7] The reaction is:

$$2HNO_3(g) + NO(g) \rightarrow 3NO_2(g) + H_2O(g)$$

and the rate data are fitted approximately by the equation:

$$d(NO_2)/dt = k(NO)(HNO_3)(NO_2)$$

The high order reaction is further complicated by the strong catalytic effects of water vapour and surface. The temperature coefficient in the range 0 to 30°C. is negative.

Nitrites

The action of nitric acid on nitrites (the 'inversion' of nitrites) has received much attention; Abel[8] showed that the equation:

$$3NaNO_2 + 2HNO_3 \rightarrow 3NaNO_3 + 2NO + H_2O$$

is an insufficient representation of the observed facts; the consumption of nitric acid is actually more than two-thirds of a mole per mole of nitrite decomposed. This he attributed to its low reaction rate with the theoretical amount of nitrous acid, the rate of decomposition of which is directly proportional to (concentration of undissociated $HNO_2)^4$, and inversely proportional to (concentration of $NO)^2$. The reaction rate constant increases very rapidly with temperature. Later work by Popovich[9] indicated a second-order reaction, but critics[10] have claimed that his results were obtained under such conditons that they represent only a special case, whereas Abel's work was much more comprehensive.

Sodium Hydrazoate

No reaction occurs when dilute nitric acid is mixed with solutions of sodium hydrazoate. The concentrated acid, however, reacts to give a mixture of nitrous oxide, nitric oxide, nitrogen trioxide and nitrogen peroxide, the proportions varying with the reaction conditions.[11] The principal reaction is:

$$HN_3 + HNO_3 \rightarrow N_2 + 2NO + H_2O$$

followed by:

$$2NO + HNO_3 + H_2O \rightarrow 3HNO_2$$

and:

$$NO + 2HNO_3 \rightarrow 3NO_2 + H_2O$$

Some nitrous oxide is formed by the action of nitrogen peroxide and trioxide on hydrazoic acid.

Sulphur Dioxide and Hydrogen Peroxide

Sulphur dioxide reduces nitric acid at elevated temperatures to give a gas rich in nitric oxide[12]: $3SO_2 + 2HNO_3 \rightarrow H_2SO_4 + 2SO_3 + 2NO$. At 50–60°C., using acid of *d* 1·15, about 70% of the theoretical quantity of nitric oxide is formed and the gas after washing with water contains 97% of nitric oxide.[13] By reducing nitric acid vapour below 450°C. with at least 1·5 mols. of sulphur dioxide per mol. of nitric acid, nearly pure nitric oxide is obtained after washing to remove sulphur trioxide and dioxide, the main impurity being nitrogen.[14]

A Dutch patent[15] describes a continuous method of reacting sulphur dioxide with the vapour from 'flashing' 33% nitric acid, to yield after washing a gas rich in nitric oxide. Other patents[16] describe methods whereby nitric acid can be reduced by hot coke, giving mixtures of carbon monoxide and dioxide, with nitric oxide as a major constituent.

When sulphur dioxide is bubbled through ice-cold fuming nitric acid, heat is evolved and, if the temperature of the acid is kept below about 5°C., eventually nitrosylsulphuric acid crystals separate. The reaction proceeds smoothly only if more than a critical amount of nitrogen dioxide is in solution; if less than this critical amount is present, little heat is evolved until sufficient nitrogen dioxide has been formed, when a sudden and violent evolution of heat and 'nitrous fumes' occurs.[17]

When more than 50% of nitric acid is present in admixture with hydrogen peroxide the mixture is unstable, presumably owing to the formation of supercritical amounts of unstable peroxides or peracids.[18]

Hydrogen Sulphide, Sulphides and Sulphamic Acid

Hydrogen sulphide reacts with solutions of nitric acid having concentration greater than 5% after an induction period which depends on the concentration and may be shortened by the addition of oxides of nitrogen. The products formed include sulphur, sulphuric acid, nitrous acid, nitrogen peroxide, nitric oxide, nitrogen and ammonia. The initial presence of sulphuric acid increases the induction period and

15% of sulphuric acid stops the reaction with 23% nitric acid completely.[19] The oxidizing action of nitric acid on many metal sulphides, both at boiling temperatures (1–4 N. acid) and at 20–22° (6–10 N. acid), is effectively retarded by hydrazine. With molybdenum sulphide at boiling temperatures, the hydrazine exerts no protective action, although at room temperature without hydrazine the oxidation is only very slow. The sulphides may be divided into two groups according to their reactions with nitric acid:

(1) Those of lead, cadmium, tin (II) and (IV), antimony and arsenic, which evolve hydrogen sulphide, and

(2) Those of copper, bismuth and silver, which do not evolve hydrogen sulphide, but react with the nitrate ion, the solubility or reactivity decreasing in the order given.[20]

Titanium sulphide, Ti_2S, is unaffected by nitric acid in the cold, but is converted to the dioxide on boiling.[21] The iron arsenides, FeAs and $FeAs_2$, are only slowly attacked by hot nitric acid.[22]

The reaction of nitric acid with sulphamic acid affords a simple method for the preparation of nitrous oxide.[23] When 4 g. of sulphamic acid are heated with 10 c.c. of previously boiled 73% nitric acid, about one litre of pure nitrous oxide (100% yield) is produced. Nitric acid of higher concentration causes violent development of nitrous oxide. Potassium thiocyanate is oxidized by nitric acid, but the reaction is stopped by the presence of sodium hydrazoate.[24]

Hydrochloric Acid and Chlorides

A large excess of hydrochloric acid in aqueous solution at 60° reacts with nitric acid quantitatively according to the equation:

$$3HCl + HNO_3 \rightarrow NOCl + Cl_2 + 2H_2O$$

Silver sulphate has considerable catalytic action, but chlorides seem to have no effect.[25] In very dilute solution (0·01 N.) an equilibrium is set up[26] according to the equation:

$$HCl + HNO_3 \rightleftharpoons HNO_2 + HClO$$

The production of gaseous chlorine by mixing hydrochloric acid with nitric acid (60–70 wt.-%) at 100–120°C. has been patented.[27] Nitrosyl chloride and nitric acid (about 45–53 wt.-%) are also produced in the reaction and the former further reacts with nitric acid to produce more chlorine. A process for preparing chlorine dioxide safely and cheaply by moistening particles of sodium chlorate with dilute nitric acid and then passing over them a mixture of 1–2% nitrogen peroxide with 99–98% air has also been patented.[28]

The kinetics of the reaction between nitric acid vapour and crystalline sodium and potassium chlorides have been studied,[29] the reaction being, e.g.,:

$$3NaCl(\text{cryst.}) + 4HNO_3(g) \rightarrow 3NaNO_3(\text{cryst.}) + NOCl(g) + Cl_2(g) + 2H_2O(g)$$

The rate decreases rapidly as the reaction progresses and becomes zero long before all the sodium or potassium chloride is converted into nitrate. It increases with the water vapour content and falls markedly with increasing temperature. Potassium chloride reacts more quickly than the sodium salt. Microcrystals of sodium nitrate, regularly oriented on the surface of sodium chloride, have been obtained by the action of hot nitric acid on sodium chloride.[30] The orientation within a given region is constant to 0·1° and is attributed to attack on the cleavage face of the carrier salt by acid corrosion.

A saturated solution of ammonium chloride may replace the hydrochloric acid in aqua regia.[31] This mixture when heated readily transforms silver bromide, iodide and cyanide into silver chloride. Lead chromate is converted into the chloride, but the sulphate is only slightly attacked. Mercuric sulphide reacts energetically and silica is also attacked. A study[32] has been made of equilibria between the solid phase components in the reaction:

$$NH_4Cl + HNO_3 \rightarrow HCl + NH_4NO_3$$

At 100°C. the reaction is represented by the equation:

$$4HNO_3 + 3NH_4Cl \rightarrow NOCl + Cl_2 + 3N_2 + 3O + 8H_2O$$

and no ammonium nitrate is formed. Nitrates such as potassium and ammonium nitrates favour the reaction forming ammonium nitrate.

Nitric acid is reduced by ferrous, stannous and titanous salts and mechanisms for the reduction have been suggested.[33, 34] Although stannous chloride reduces nitric acid to hydroxylamine, ferrous sulphate (a weaker reducing agent) and titanous chloride (a stronger reducing agent) give nitric oxide only.[35] A freshly prepared solution of a mixture of nitric and nitrous acids oxidizes stannous ions, but the oxidizing activity gradually decreases to zero.[36] The solution can be reactivated by diluting it with water, and it is concluded that the nitrous acid promotes the reaction with nitric acid. In the reduction of nitric acid to nitric oxide by ferrous chloride, molybdic acid acts as a powerful positive catalyst,[37] probably by its transformation into molybdenum pentachloride which is the true active agent. Vanadous sulphate liberates nitrous fumes from nitric acid.[38] At 0°C. the formal oxidation potential for the reaction $Co^{+++} + e \rightarrow Co^{++}$ is 1·800 v. in 1 M. and 1·816 v. in 4 M. nitric acid and at 25° 1·842 v. in 3 M., and 1·850 v. in 4 M., acid.[39]

Phosphorous and Arsenious Acids

Nitric acid free from oxides of nitrogen has no action on phosphorous acid.[40] In 55% nitric acid containing oxides of nitrogen, the oxidation of phosphorous acid is complete in 15 min. at 100°; under similar conditions with 44, 31 and 17% nitric acid, 4, 93 and 100% respectively of the phosphorous acid is unchanged. Arsenious oxide is oxidized by nitric acid. Mercury has an inhibiting effect on the reaction, but this can be counteracted by the addition of potassium iodate or hydrochloric acid, the former being preferred.[41, 42] The kinetics of the gross reaction:

$$3H_2AsO_3 + 2HNO_3 \rightarrow 3H_3AsO_4 + 2NO + H_2O$$

were examined by Abel, Schmidt and Weiss[43]; the rate of oxidation is proportional to the concentration of the arsenious acid and to the (concentration of nitrous acid)^2. The oxidation of the nitrous acid proceeds *via* dinitrogen trioxide; nitrous acid functions through parallel reactions, first as an autocatalyst and secondly as a source of the intermediate oxidant dinitrogen trioxide. Thus the rate-determining step is:

$$N_2O_3 + H_3AsO_3 \rightarrow H_3AsO_4 + 2NO$$

The oxidation of arsenious acid by nitric acid is accelerated by nitrous acid and by chloride impurities.[44]

Electrolytic Reductions

When nitric acid solutions are electrolyzed between platinum electrodes[45] there are two alternative reactions, either of which can predominate at the cathode:

(1) reduction of nitric acid to nitrous acid,

(2) evolution of hydrogen.

Reaction (1) is strongly autocatalytic, the current density that it can maintain being determined by the nitrous acid concentration established at the cathode surface. This dependence accounts for the observed variations of cathode potential during electrolysis under various conditions, and may account for the catalytic action of nitrous acid on the solution of certain metals in nitric acid. It has been observed that nitrogen gas can be formed during electrolytic reduction of the nitrate ion.[46]

Using a mercury cathode in sulphuric acid[47] nitric acid can be electrolytically reduced to hydroxylamine, the following conditions being suggested: current density 0·25 amp. per sq. cm; current concentration 10 amp. per litre; temperature 14–16°C.; nitric acid concentration kept at N. by continuous addition; sulphuric acid concentration 15 N. at the start, decreasing to 3 N. at the end of the run. After removal of unconverted nitric acid, hydroxylamine sulphate can be crystallized out. During the electrolysis, some *iso*monosulphohydroxylamine sulphate, $(NH_2OSO_3H)_2H_2SO_4$, is formed. In a modified preparation[48] nitric acid is reduced at an agitated mercury cathode in an apparatus provided with cooling and fitted with lead anodes. Using as high a c.d. as possible without excessive heating, e.g. 10 amp./sq. dm., hydroxylamine concentrations up to 75–100 g./litre can be obtained before its reduction to ammonia becomes excessive. The yield based on nitric acid is 75–78%. Other workers[49] have preferred lead dioxide as an anode material and concentrated hydrochloric acid as catholyte. Under these conditions, when hydrogen chloride gas is passed through the cooled reduced catholyte, hydroxylamine hydrochloride separates out. As a result of studies with platinum, mercury and copper cathodes in phosphoric acid and of mercury in sulphuric acid, the scheme for the reaction mechanism shown in Fig. 1 has been suggested.[50]

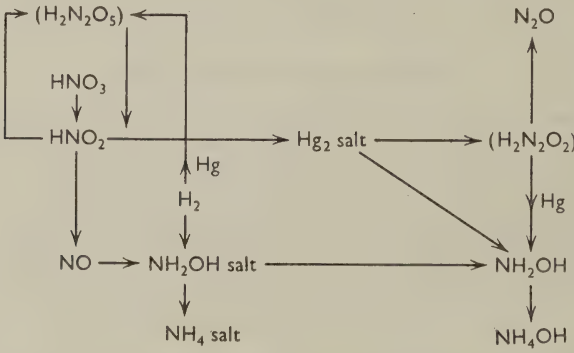

FIG. 1.—Suggested reaction scheme for electrolytic reduction of nitric acid.[50] (Formulae of uncertain intermediates are shown in parentheses)

The compounds following one another are reduced in acid solution with increasing cathodic potential. Down to NO, the reduction proceeds without evolution of hydrogen. Formulae of uncertain intermediate products are enclosed in brackets. When a graphite anode is used for electrolytic reduction of nitric acid, the anode can disintegrate explosively[51, 52]; this has been attributed to the development of oxygen under pressure in the pores of the carbon or to the formation of graphitic oxide.

Some anomalies in the oxidation–reduction behaviour of nitric acid have been observed[53]: a solution of the acid in which vanadium has been dissolved contains quadrivalent vanadium; on evaporation to dryness, vanadium pentoxide results, although it has a greater oxidation potential than nitric acid. Similarly nitric acid converts thallium to thallous ions and iridium to quadrivalent ions, yet on evaporating these solutions to dryness trivalent thallium and pentavalent iridium result, although they too, have oxidation potentials greater than nitric acid. Repeated treatment of chromium with nitric acid and evaporation of the resulting solution to dryness yields some dichromate ($HCrO_4^-$), yet this is a stronger oxidant than nitric acid.

The oxidation potential of nitric acid irradiated by *X*-rays has been examined.[54]

REACTIONS WITH NON-METALS

The Halogens

Ruff and Kwasnik[55] have described the preparation of fluorine nitrate from nitric acid and free fluorine. The use of acid having concentration greater than 3 N. decreases the danger of explosion and the risk disappears when 100% acid is used. Purified fluorine was bubbled through 100% acid and the reaction product was purified by distillation in a quartz column at 100 mm. Hg. The initial cut was silicon tetrafluoride; pure fluorine nitrate came over at −79° and the higher cuts contained fluosilicic acid and hydrogen fluoride. The conversion to fluorine nitrate was nearly quantitative at 20°C., but was incomplete at lower temperatures. Fluorine nitrate is a possible war gas. The same compound may be formed when fluorine and solid potassium nitrate react together.[56]

Aqueous nitric acid reacts with gaseous fluorine according to the equation:

$$2HNO_3 + F_2 \rightarrow N_2O_6 + 2HF$$

If the reaction is carried out for short times at low temperatures it is possible to detect the presence of a very unstable, pungent peracid, supposedly HNO_4.[57] Trifonov[58] suggested that this transient substance could result from the reaction:

$$N_2O_6 + H_2O \rightarrow HNO_3 + HNO_4$$

and decompose by the process:

$$HNO_4 + H_2O \rightarrow HNO_3 + H_2O_2 \rightarrow HNO_3 + H_2O + \tfrac{1}{2}O_2$$

The maximum yield of pernitric acid is obtained only with dilute nitric acid (1·3 N.), but in general the yields obtained are very irregular, partly because much of the dinitrogen sesquioxide is lost to the gas phase and partly because of the instability of the per-acid.

When fuming nitric acid is kept in contact with chlorine gas for one month at 15–18°C. chloric acid ($HClO_3$) and nitrogen peroxide are formed. Similarly, when a bulb of bromine is connected via a U-tube to a bulb of fuming nitric acid, bromine vapours slowly distil towards the acid, which acquires a deep red colour. Bromic acid ($HBrO_3$) is formed.

When the vapours of fuming nitric acid are allowed to react with iodine crystals,[59] iodic acid is deposited both on the iodine and in the acid. Ball and Singh[60] considered the primary product obtained by triturating iodine with fuming nitric acid to be iodine tetroxide, I_2O_4, which in contact with moisture is decomposed into iodine pentoxide and iodine. Heat accelerated the decomposition into the pentoxide.

Sulphur and Selenium; Phosphorus, Arsenic and Antimony

Neither sulphur nor tellurium is affected when exposed for two months at 15–18°C. to the vapours of fuming nitric acid.[59] Both varieties of selenium are transformed at the end of a month into selenium dioxide. Arsenic and antimony react feebly under similar conditions, because of the protective oxide formed, but pulverized arsenic at the end of a month is partially oxidized to arsenic trioxide. Pulverized antimony is much less affected. Phosphorus reacts under these conditions to give a mixture of phosphorous and phosphoric acids which gradually changes to phosphoric acid.

Sulphur is oxidized by hot mixtures of sulphuric and nitric acids. The rate of oxidation increases with temperature; at a given temperature it decreases with increasing percentages of sulphuric acid in the mixture, e.g., at 80°C., up to 80% H_2SO_4 with 5·6% nitric acid; it then increases to a maximum, e.g., for 80°C., at 90·4% H_2SO_4. The relative proportions of the sulphur dioxide and sulphuric acid produced depend on the concentration of sulphuric acid in the mixture, the area of exposed sulphur and the temperature. It is postulated that the oxidant is a cation, e.g., NO_2^+, $NO_3H_2^+$ or $N(OH)_3^{++}$ rather than the nitrate ion.[61]

The fuel gases from the complex gasification of fuels and phosphorite in a blast furnace, using an air blast enriched with oxygen, contain phosphorus and phosphine. These can be removed by the method of Rozenkrants and Dembo[62] in which the gas is scrubbed at 60–70° with 42% nitric acid. A cloud of phosphoric acid is formed rapidly and absorbed somewhat more slowly by the nitric acid. Carbon monoxide and hydrogen are not affected. A similar process can be used to free the gas produced in the electro-distillation of phosphorus from phosphorus and phosphine.

The reactions of carbon with nitric acid are discussed under 'Organic Reactions' (p. 330). Dilute nitric acid decomposes silicon ditelluride.[63]

CORROSION OF NON-METALLIC MATERIALS OF CONSTRUCTION

Concrete, Stone, Enamel

Nitric acid is a powerfully corrosive reagent affecting many materials of construction other than metals. It attacks concrete by forming soluble salts with the calcium hydroxide present to some extent in all concretes.[64] The calcareous stone of monuments is attacked by nitrous and nitric acids formed from the air by nitrifying bacteria, which use carbonate as a source of carbon.[65] The soluble salts so produced are washed away by rain. Recipes have been given[66,67] for acid-resisting cements.

Non-acid-resisting enamels are attacked by concentrated nitric acid. 'Acid-resistant white cover' enamels, which are very resistant to inorganic and organic acids at room temperature, are attacked to a moderate extent by boiling nitric acid. 'Acid-proof' or 'chemical' enamel is about three times as resistant to acid attack at boiling temperature as the acid-resistant white cover enamels.[68] The comparative solubilities of a number of typical acid-resisting materials in nitric acid of various concentrations have been surveyed by Muravlev[69]; their acid resistance generally increased with increase in the alumina content and with decrease in the contents of ferric oxide, lime and magnesia.

Glass

Several authors have reported the action of nitric acid on glass.[70, 71] Turner and Wilson[72] found acid of d 1·2 had little effect on three types (two English, one French) of chemical glassware, when kept in contact with the glass for three hours at 100°C. Nagaeda made a detailed study of the durability of glasses of the high barium and high lead series.[73] The effect of temperature on the durability was studied by carrying out a 'staining test' at 30–80°. Polished pieces of glass were immersed in acid of various concentrations and the time t was measured for formation of a film of silicate gel of such a thickness on the surface that the interference colour of reflected light of the first order from the surface of the glass changed from blue to purple. This time was much longer with glass rich in lead oxide than with glass rich in barium oxide. The production of the film was greatly accelerated by an increase in temperature. The effect of 0·005–5 N. nitric acid was determined from 30–70°C. The results showed that the relation between t and N., where N is the normality of the acid, for values of N between 0·5 N. and 2 N. is expressed by the following equations:

$$\mathrm{N} = n - mt$$

$$a = bt + \log \mathrm{N}$$

$$Kt + X = \mathrm{N} \log \mathrm{N}/(\mathrm{N} - X)$$

where n, m, a, b, K and X are constants. In the third equation, K and X are, respectively, the reaction constant and the amount of alkali salt dissolved in time t.

Mixtures of nitric with sulphuric and hydrochloric acids showed the average value of the film-forming power of each acid. The velocity at which a thin film formed on the surface of glasses rich in barium and lead oxides when treated with 0·1 N. nitric acid at 23–60°C. was studied by measuring the time t required to cause a specified change in the interference colour. A relation $f^2 = Ct + D$ was found, where f is the thickness of the film and C and D are constants which vary with the kind of glass and the temperature. Substitution of lead oxide for barium oxide increased the acid resistance of a glass, while substitution of barium oxide or boron trioxide for silica decreased it. Concentrated nitric acid did not cause any appreciable attack. A comparison of the corrosion and abrasion resistance properties of various glasses has also been made,[74] by means of diffusometer and reflectometer measurements. Aluminium titanate is attacked only slowly by cold mineral acids, including nitric acid, and, having a small coefficient of expansion, its use for making glass and ceramic ware has been considered.[75]

Molybdenum disilicide shows excellent resistance to nitric acid[76]; recipes for nitric acid-resistant cement have been given.[77–8] Polythene is slowly attacked by 68% nitric acid at 50°C.[79]; the action of the acid on plasticized polyvinyl chloride has been noted[80, 81] and a recipe for a nitric acid pump lubricant incorporates a ‘substantially saturated aliphatic hydrocarbon polymer’.[82]

ACID REACTIONS

Acid Strength

The ‘strength’ of nitric acid has been compared with that of other acids, by measuring the effect of each acid on the rate of sugar inversion in aqueous solution[83]; the activity so found is related to the stability of the oxonium compounds (e.g., H_3O^+) formed. The activities decrease in the order:

$$HClO_4 > HBr > HSO_3C_6H_5 > HCl > HNO_3 > CH_3CO_2H > CHCl_2CO_2H$$

The catalytic action of hydrobromic, hydrochloric and nitric acids on the decomposition of diazoacetic ester follows the same order. The catalytic effect of nitric acid on the hydrolysis of hypophosphoric acid has shown that, unlike other strong acids, the activity of nitric acid does not increase so sharply with concentration, and even decreases at the higher concentrations.[84]

In solvents such as diethyl ether, where solvation is less marked, the differences between the acids are greatly increased. Studies of the effects of nitric acid on the partial pressure of diethyl ether over mixtures of the two[85] show that a 1:1 complex is formed when half a mole fraction of the acid is present. The dissociation constants of nitric acid in methyl and ethyl alcohols have been measured.[86]

The displacement of tungstic acid by nitric acid has been investigated.[87]

Production of Ammonium and Potassium Nitrate

The reaction between nitric acid and ammonia is of great industrial importance in the production of large tonnages of ammonium nitrate, chiefly for fertilizer and explosive uses (see p. 336). A patent by Stengel[88] describes how ammonia gas is caused to react continuously with nitric acid in a packed vessel under such temperature conditions (180–250°C.) that the products are molten ammonium nitrate and steam. The water content of the ammonium nitrate produced depends on the reaction temperature. When 62% nitric acid is the starting material, the water content of the product produced at various temperatures is: 190°C., 40%; 225°C., 0·5%; 265°C., 0·2% (95% of the acid converted) and 300°C., 0·1% (80% of the acid converted). A study of the rate of absorption of ammonia in acids, including nitric, has been made.[89] (See also Vol. VIII, Suppl. 1, p. 506.)

Leucite is attacked by nitric acid yielding potassium nitrate and the process has been extensively investigated and reviewed by Blanc.[90, 91] The leucite is first crushed and purified by physical means and then acidified with hydrochloric or nitric acid. In the latter case solutions containing aluminium and potassium nitrates result, separation of the salts being based on the relative insolubility of aluminium nitrate in cold 65–70% nitric acid. The ferric nitrate remains in solution under these conditions and the crystallized aluminium nitrate contains only a trace of iron. It may subsequently be processed to give alumina. The process is of great potential importance in Italy, where the lava masses of six extinct volcanoes have been estimated to contain over 100,000 million tons of material representing nearly 9000 million tons of potash.[92] Other related processes involving reaction between nitric acid and leucite or similar minerals have been patented.[93, 94] The alumina in clay may also be attacked with nitric acid, the rate being similar to that obtained with sulphuric acid under similar conditions.[95]

Production of 'Superphosphate' Fertilizers

Many investigations have been made into the use of nitric acid to replace wholly or partly the sulphuric acid consumed in making fertilizers of the superphosphate type and numerous processes have been evolved. In one process 100 parts of crude phosphate (containing 29·4% P_2O_5 and 47·2% CaO) are decomposed with 203 parts of 47% nitric acid. The excess of nitric acid and that formed in the reaction:

$$CaH_4(PO_4)_2 + Ca(NO_3)_2 \rightarrow 2CaHPO_4 + 2HNO_3$$

are removed by evaporation; $CaH_4(PO_4)_2$ and calcium nitrate solution are then obtained by extracting the product with water.[96] In another process the nitrated phosphate rock is treated with potassium chloride and granulated,[97] and numerous variations are reported.[98–117] The relative amounts of water-soluble, citrate-soluble and insoluble phosphorus compounds formed from crude calcium phosphate have been measured[118] and a continuous nitration process has been patented.[119] The presence of hygroscopic calcium nitrate in the product can be avoided either by using a mixture of nitric and sulphuric acids to solubilize the phosphorus compounds in the rock[120] or by adding carbon dioxide.[121] Fertilizers of higher nitrogen content may be produced by adding urea,[122, 123, 124] or by ammoniating the nitrated phosphate, drying and granulating. The latter product has exhibited a favourable effect in tests of crop response, storage and drillability.[126] Comparisons of the various processes have been made[127, 128, 129, 130] and the system $Ca(NO_3)_2$–HNO_3–H_3PO_4–$Ca_3(PO_4)_2$–H_2O has been studied.[131] Nitric acid has also been applied directly on field and vegetable crops as a fertilizer with promising results.[132] It has also been used to remove nickel, cobalt, manganese and aluminium components from iron ores.[133]

REACTIONS WITH METALS

General

The reactions of nitric acid with metals are of considerable importance and have long exercised the minds and hands of chemists. Attempts to generalize the results of such interactions have been made by Abel[134] and others.[135, 137, 138] Abel suggested the following processes, where M is the metal:

$$3M + nNO_3^- + 4nH^+ \rightarrow 3M^{n+} + nNO + 2nH_2O \qquad (I)$$

and

$$2M + nNO_3^- + 3nH^+ \rightarrow 2M^{n+} + nHNO_2 + nH_2O \qquad (II)$$

These two independent reactions can then be combined to $(A) = I - II$ (reduction of nitrous acid to nitric oxide) and to $(B) = 1/n(3II - 2I)$ (reduction of nitric acid to nitric oxide and nitrous acid). The reactions depend on the physical conditions prevailing, including diffusion and agitation, so that the system is complicated. Tillu[135] proposed that when the products of reaction are the metal nitrate, water and oxides and hydrides of nitrogen; the equation takes the following form:

$$2(nM/v) + 2(n+1)HNO_3 \rightarrow 2(nM/v)(NO_3)_v + (n+1)H_2O + N_2O_x$$

In this formula M is the metal, v its valency, and n and x are two integers (positive, negative or zero) such that $x = 5 - n$.

Nitric acid is handled industrially on a very large scale, and it is therefore not surprising that there is much published work on the corrosion resistance of numerous metals and alloys. The detailed consideration of this topic is beyond the scope of this work, but several useful reviews and lists of data are available.[139–148] Corrosion by red fuming nitric acid has also been studied,[149] certain stainless steels, tin, gold and tantalum being resistant to attack. Ferrous salts accelerate the solution of many metals and alloys in nitric acid and this is attributed to the formation of nitrous acid which dissolves the metal more rapidly. Oxidizing agents may reduce the rate of solution by removing nitrous acid. A 1:1 alloy of copper and nickel dissolves in nitric acid in periodic fashion, the reaction periods being of diminishing length.[151] Urea and hydrazine retard the oxidation of metals by nitric acid; it is suggested that the effectiveness of ammonia as a retarding agent is due to the formation of hydrazine.[152] The corrosivity of nitric–acetic acid mixtures towards steels has been studied[153]; there is evidence for the formation of a slightly stable compound of formula CH_3CO_2H,HNO_3. In the following paragraphs recently acquired knowledge of the action of nitric acid on the metals is presented.

Lithium, Copper, Silver

The velocity of reaction of lithium with nitric acid has been reported.[154] The rate of solution of copper and silver can be decreased by rotating the specimen, though this decrease can be prevented by adding 1% of sodium nitrite to the solution, thus destroying the passive film.[155, 156] Many measurements of the rate of solution of copper in nitric acid are available; it is proportional to the concentration of acid up to 4 N., being 'insignificant' in acid of less than 3 N. strength,[157] but increases rapidly at higher concentrations.[158, 159] Either copper ions or nitrous acid may act autocatalytically. Because the temperature coefficient of the reaction above 30°C.[160] is very high, it has been suggested that overall solution is a function of minute electrochemical reactions on the surface of the metal involving local potential differences.[161] Berg considered the velocity of reaction to depend on the concentration of undissociated acid.[162]

Russian work,[163] using both stationary and rotating copper discs, proposes a chain mechanism, starting with the oxidation of the metal by traces of nitrogen dioxide:

$$Cu + NO_2 \rightarrow CuO + NO + 23{\cdot}68 \text{ g.-cal.}$$

In nitric acid free from nitrogen dioxide, solution does not occur as long as the acid is protected from decomposition. It is suggested that the heat of oxidation of the copper activates nitric acid molecules, which, on reaction with nitrous acid present, produce new active centres in the form of nitrogen dioxide:

$$HNO_3^* + HNO_2 \rightarrow H_2O + 2NO_2 + 14{\cdot}00 \text{ g.-cal.}$$

Since free NO_2 exists only in concentrated nitric acid, in dilute solutions an induction period is observed before the metal dissolves. The reaction chain may be broken in strong nitric acid, where nitrous acid is less plentiful; then surface oxidation by nitrogen dioxide occurs so rapidly that the metal becomes covered with a thick cupric oxide film, leading to a sharply decreased reaction rate. The proposed reaction scheme explains also the inversion of copper dissolution kinetic curves, the inhibiting effects of impurities and the ageing effect of nitric acid solutions. (See also Pinner's work.[164])

The effect of ultrasonic vibrations on the solution of copper in nitric acid, under conditions where a diffusion process is dominant, is comparable to that of rotating the metal.[165] In hydrochloric–nitric acid mixtures, photosensitive films form on copper.[166] The effect of nitric acid on the solution of the metal in nitrous acid has been examined.[167] The reaction is accelerated by oxidizing substances, but colloidal materials, surface-active compounds (alcohols, organic acids and amines), urea, pyridine, quinoline and potassium halides other than the iodide, retard the reaction.[168]

The velocity with which 32·4% nitric acid attacks silver–gold alloys is determined chiefly by the silver content of the alloy[169, 170] and follows the equation $p = \phi(t/a)$ where p is the % of the total silver dissolved at time t.[171]

The action of nitric acid on copper–silver and silver–gold solid solutions has given results which confirm that stress corrosion is triggered off by electrochemical processes.[172]

Alloys of silver (13–60%), palladium and platinum resistant to nitric acid have been patented[173] and data on the reaction with nitric acid of a related alloy in which gold replaces platinum (40% silver, 30% gold, 30% palladium) are available.[174, 175]

Zinc, Cadmium, Mercury

Hydrogen is evolved when zinc is dissolved in dilute nitric acid in the presence of platinum. In the absence of platinum, the hydrogen atoms reduce nitric acid. If the concentration of acid is increased, the amounts of hydrogen and nitrogen produced decrease, the amount of nitric oxide remains about the same, and the amounts of ammonia and nitrous oxide increase.[176] The latter results from reaction between hydroxylamine and nitrous acid[177]:

$$NH_2OH + HNO_2 \rightarrow N_2O + 2H_2O$$

The relative importance of the reactions:

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2 \qquad (I)$$

and

$$Zn + HNO_3 \rightarrow ZnO + HNO_2 \qquad (II)$$

when zinc is dissolved in dilute nitric acid was examined by altering the ratio of hydrogen ion to nitrate ion by using mixtures of nitric and sulphuric acids. With 0·5% of nitric acid in 10% sulphuric acid, hydroxylamine equivalent in amount to 2–5% of the zinc was obtained, but no nitrous oxide was formed. This indicates that reaction I is predominant and this conclusion was supported by other observations.[178] In a study[179] of the etching of zincographic plates (zinc 98·98, lead 0·9, cadmium 0·1, iron 0·02%) the rate of solution in acid of up to 25% concentration was determined by the hydrogen ion concentration. The course of the reaction is represented by the equations:

$$Zn + 2H^+ \rightarrow Zn^{++} + 2H$$

$$8H + HNO_3 \rightarrow NH_3 + 3H_2O$$

and

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

At higher acid concentrations the reaction followed the scheme:

$$3Zn + 2HNO_3 \rightarrow 2NO + H_2O + 3ZnO \xrightarrow{6HNO_3} 2NO + 4H_2O + 3Zn(NO_3)_2$$

The solution-body phenomenon and anisotropy of solution rate of single zinc crystals in concentrated nitric acid have been studied; close correspondence is found between directional solution rates in zinc and bismuth.[180]

Recent corrosion data have been published[181–184] and a recipe has been given for procuring a corrosion resistant zinc surface.[185]

When cadmium is dissolved in 2, 5 or 10% nitric acid in the presence of platinum only very small amounts of hydrogen are evolved. The amount of ammonia formed is only half of that formed when zinc is dissolved, but the amounts of nitrous acid, nitric oxide and nitrous oxide are larger.[186, 187]

When cadmium was dissolved in mixtures of nitric and sulphuric acids having various ratios of hydrogen ion to nitrate ion, more hydrogen and ammonia were formed than with nitric acid alone. The direct reduction of nitric acid was more pronounced than in the solution of zinc. Thus the two primary reactions:

$$Cd + 2H^+ \rightarrow Cd^{++} + H_2$$

and

$$Cd + HNO_3 \rightarrow CdO + HNO_2$$

must occur at comparable rates.[188]

Indian work on the solution of mercury in nitric acid has shown that the reaction proceeds in two stages: (*a*) the formation of mercurous ions, and (*b*) their oxidation to mercuric ions accompanied by the formation of nitric oxide and mercuric nitrite; formation of mercuric nitrite is catalyzed by various metal ions.[189] Both stages are accelerated by formic or nitrous acid, but inhibited when the latter is removed by urea; nitrous acid is always the first reaction product.[190] Passivity is observed in stirred systems, more in dilute than in concentrated solutions. Later work,[191] exploring this passivity, suggests that nitrous acid is the dissolving agent and that the initial nitrous acid results from catalytic decomposition of nitric acid on the mercury surface, where an oxygen adsorption complex forms.

Aluminium

The action of nitric acid on 99·5% aluminium does not appear to be influenced by diffusion. The solution velocity is doubled for every 10°C. rise in temperature; the maximum solution rate occurs in 5–6 N. acid, falling almost to zero in acid stronger than 20 N.[192] Aluminium equipment is suitable[193] for chloride-free 95, 75 and 55% acid, but not for 20 or 40% acid. The addition of urea, ammonium nitrate or chlorine, which remove nitrous acid, has no effect on the solution velocity; it is inferred that nitric acid acts purely as an acid towards the metal. There is a close relationship between acid pH and solution velocity. Up to 50°C. uniform corrosion occurs, but not at or near welds in the metal. Above this temperature attack occurs adjacent to welds. As little as 0·1% of hydrofluoric acid inhibits corrosion by red fuming nitric acid at 70°C.[194] The oxide films formed on the metal are not acid-proof, although it is claimed that annealed pure metal, because it is attacked less than rolled pure metal, has the less disturbed oxide film.[195] Information is available on anodic control as a method of protecting aluminium in nitric acid.[196–198]

A detailed account[199] of the corrosion by nitric acid at various concentrations and temperatures of aluminium containing various amounts of silicon, iron and manganese shows that solution is greatest during the first hour, but falls considerably after five hours. Above 40°C. corrosion in acids of medium strength, and to some extent in weak and very strong acid, increases sharply. In general, solution decreases with increasing purity of the aluminium[200]; attack is chiefly at grain boundaries, increasing with the separation of intermetallic components there, but after-treatment of sheet metal may slow solution. The effects of various metallurgical operations on the corrosivity of aluminium have been described.[201, 202] Nitric acid attack on refined aluminium containing titanium and boron has been studied.[203]

The formation of dinitrogen trioxide, shown by a deep blue colour, has been observed in nitric acid solutions in contact with aluminium.[204] Acid attack can be inhibited by 0·1–5% of chromate ions,[205] and 1% nicotinic acid slows acid attack on aluminium and its alloy with 5% magnesium.[206] The effects of sulphuric–nitric acid mixtures on aluminium are greater than those of nitric acid alone.[207–209] The behaviour of aluminium–zinc alloys in nitric acid has been examined.[210] An aluminium anode ('sacrificial anode') can be used to protect stainless steel from nitric acid attack,[197] while aluminium can be diffused into steel at 1000°C. to improve the resistance to nitric acid.[211]

Germanium, Tin, Lead

The electrical properties of germanium for use in transistors are improved by etching with nitric acid[212, 213] in solution with a polyhydroxy compound, e.g., sugar, glycols. The formation of 'electron holes' on germanium surfaces has been demonstrated by an experiment in which the point of a platinum wire is surrounded with a drop of nitric acid and is in contact with a germanium plate.[214] At the contact point, a current is produced by the discharge of positive ions on the wire; this charge is distributed in the form of 'electron holes' in the germanium, and intensive surface oxidation follows. The germanium dioxide formed is sparingly soluble in the acid, and forms around the point a dark-grey ring, the diameter of which is proportional to the life-time of the holes.

The rate of reaction between tin and 10–64·5% nitric acid appears to be controlled by the rate of decomposition of nitrate ion or by diffusion of nitric acid. The diffusion process increases in importance as the concentration of the acid is increased, but in solutions containing more than 80% of acid the tin becomes passive.[215] Lithium, sodium and potassium iodides retard the action of nitric acid on tin.[216] The products of the acid attack with acid in excess are stannous and stannic ions, nitric oxide, nitrous oxide, nitrogen, ammonia and hydroxylamine. The amounts of stannic ions and gaseous products increase and the amounts of stannous ions, ammonia and hydroxylamine decrease with increasing temperature or concentration of acid.[217, 218]

A 65% tin–35% nickel alloy, deposited by electrolysis of a chloride–fluoride bath on to iron or copper, gives a hard plating; its resistance to nitric acid has been examined.[219]

The corrosive effect of nitric acid on lead increases with its concentration[220] but apparently decreases in very concentrated acid. The presence of antimony and copper in lead increases corrosion.[221] A lead–palladium alloy, containing more than *ca.* 37% of palladium, resists the attack of 1 N. nitric acid when the metal is used as an anode.[222] The anodic behaviour of silver–lead alloys in nitric acid has been studied.[223] A chemical polishing solution for tin, lead and alloys contains concentrated nitric acid, ammonium fluoride and fluosilicic acid.[224]

Titanium, Zirconium, Hafnium

Annealed titanium resists both concentrated and fuming nitric acid at room temperatures[225]; however, explosions have been reported[226, 227] as having arisen from the action of red fuming nitric acid on the metal and alloys. Boiling 65% nitric acid attacks titanium 'at a rate of over 0·005 inch per year'.[228] Anodized titanium resists nitric and nitric–sulphuric acid mixtures, hot or cold.[229] The important advantages of this metal in chemical industry have been reviewed.[230] Passive surfaces and the formation of protective films have been observed, using electron diffraction techniques on metal attacked by boiling acid.[231] The acid-resistance of alloys of titanium with aluminium decreases with increasing aluminium content[232]; the low-grade spongy metal made by the Kroll process has a composition similar to a titanium–iron binary alloy, and this seems to be about as resistant as pure titanium.[233]

Zirconium and its alloys resist all concentrations of nitric acid; fuming acid produces a protective surface oxide film.[234, 236] Addition of hydrofluoric acid aids solution.[235] An increase in the normally small amounts of oxygen, carbon, nitrogen and hafnium present as impurities decreases the resistance of zirconium towards nitric acid.[234]

Hafnium in 70% nitric acid at room temperature develops an anodic film over the crystal, the film thickness depending on the crystal orientation.[237]

Bismuth, Vanadium, Niobium, Tantalum

The solution-body phenomena and anisotropy of solution rate of bismuth in nitric acid have been examined.[238]

Nothing seems to be known of the resistance of vanadium or niobium to attack by nitric acid, probably because the pure metals are rarely used; they are usually employed as additives, e.g., in stainless steel (*q.v.*), where they combine with the carbon present. The resistance of steel to 50% nitric acid may be improved by saturating the surface with vanadium deposited from the gas phase.[239] No improvement in resistance to nitric acid is achieved when niobium is similarly diffused into steel.[240] Niobium germanides do not react with nitric acid.[241]

Tantalum and its alloys with molybdenum have been tested with nitric acid[242]; tantalum and tantalum-rich alloys are unattacked, and molybdenum-rich alloys form a protective film.

Chromium, Molybdenum, Tungsten, Uranium

The corrosion of chromium (98·9% pure) by nitric acid of various concentrations, in the presence and in the absence of dichromate ions, increases with temperature and with acid and dichromate concentrations.[243]

Reactions of pure molybdenum with nitric acid have not been reported; for those of alloys, see stainless steel. Molybdenum–germanium compounds[244] dissolve readily in nitric acid.

Diffusion of chromium,[245, 246] molybdenum[247] and tungsten,[248] singly or severally, into steel and into nickel and its alloys gives coatings which resist corrosion by nitric acid.

Uranium and its alloys have received considerable study in recent years; in particular, the recovery of uranium in 'spent' fuel elements from atomic reactors is usually accomplished by solution in nitric acid. The solution of uranium–aluminium alloys in nitric acid is catalyzed by mercury[249]; uranium–zirconium alloys may be safely dissolved in a mixture of nitric and hydrofluoric acid to which aluminium nitrate is added.[250]

Manganese, Iron, Steel, Nickel, Palladium, Platinum

A film of manganese deposited on steel shows poor corrosion resistance towards 50% nitric acid.[251]

The curve relating rate of solution, V, of iron containing 0·18% of carbon, 0·14% of silicon, 0·4% of manganese, 0·027% of sulphur and 0·017% of phosphorus to the concentration (S) of nitric acid has a maximum V at $S = 6{\cdot}8$ N.; at $S = 13$ N., $V = 0$, i.e., the metal is passivated. The value of V increases with stirring and with temperature, the temperature coefficient being 1·1–1·2; an increase in S causes the electrode potential of the iron to shift first to the negative side and at $S = 0{\cdot}01$ N. to the positive side.[252] Values of V for various values of S at 25°C. have been given for an unspecified sample of 'iron'; they do not coincide with the data above.[253] It must be realized that impurities in iron and its past treatment both have considerable effects on the behaviour of the metal towards nitric acid.[254–273]

It has been thought that the passive film formed on iron by nitric acid is ferric oxide; it can be removed by whirling the metal in nitric acid for about 30 seconds at 3000 r.p.m.[274] Later work[275] gave rise to the opinion that the passive film is ferric acid or a related higher valency iron compound which, when decomposed to ferric oxide, is calculated to be 40–125 A. thick. The 'higher-valency compound' is formed at anodic areas of the metal, being chemisorbed when a critical concentration is reached, and thereby stabilized. It can be broken down by cathodic reduction, mechanical shock or by the presence of halide ions. A useful discussion of iron passivation has been given.[276] Electrochemical investigations into the etching of iron monocrystals have been made.[277–279] Confirmation of the film theories above has been found in studies of the photogalvanic effect shown by passive iron.[280]

Criteria for the composition of nitric acid-resistant cast iron have been given; the manganese content must be as low as possible.[281] The corrosion and passivation of iron in sulphuric–nitric acid mixtures have been studied.[282, 283]

The resistance of the numerous varieties of stainless steel towards nitric acid has a vast literature. For information on the behaviour of a specific type of steel the reader is referred to the following:

(1) The publications of the American Society for Testing Materials.
(2) 'Stainless Iron and Steel', J. H. Moneypenny (Chapman and Hall), 1954 and 1959.

(3) 'Chromium and Nickel Austenitic Steels', ed. F. H. Keating (Butterworth), 1956.

The types of stainless steel most commonly used for containing nitric acid are:

(*a*) '18/8/Ti' which contains 18% of chromium, 8% of nickel and about six times by weight as much titanium as carbon, the carbon content being 0·05–0·1%.

(*b*) A steel containing 18% of chromium, 10% of nickel, and about ten times as much niobium as carbon, the carbon content being 0·05–0·1%.

(*c*) 'Extra-low carbon' steel which contains 18% of chromium, 10% of nickel and not more than 0·03% of carbon.

These three types of steel resist nitric acid of greater than about 90% concentration up to *ca.* 50°C.; acid of concentration not greater than 68% is resisted up to 80–90°C.; boiling 30% nitric acid attacks them at *ca.* 0·1 mm./year. Nitric acid of any concentration is resisted by these steels at room temperatures.

The passivation[284–286] and anti-corrosive treatment[287] of plain and stainless steels have been studied. The most effective inhibitors of nitric acid attack on plain steel are palmitic acid[288] and phosphate[289, 290] films; inhibition is also achieved with potassium chromate, permanganate, iodide, bromide, chloride, sodium sulphide, sulphite and thiosulphate and with thiourea.[291]

The rate of solution of nickel in nitric acid has been measured between 0° and 65°C. for acid concentrations between 0·25 N. and 14·5 N.[292] Below 3·5 N. the rate of solution is proportional to the square root of the concentration; at high acid concentrations the rate equation is a complex function, and results are difficult to reproduce.

The effect of aqueous and weak alcoholic nitric acid on alloys of nickel with titanium and chromium,[293] and with several transition metals,[294] has been noted.

Palladium has been reported to dissolve more rapidly in 10 N. than in weaker nitric acid.[295]

Platinum, widely used in the laboratory for containing hot concentrated nitric acid, e.g., in oxidizing organic residues, would seem to be unaffected by nitric acid of any concentration. The effect of platinum on the resistance of precious metal alloys is discussed in the paragraphs dealing with those metals.

ADDITION COMPOUNDS OF NITRIC ACID

With Sulphur Trioxide

Investigation of the physicochemical properties of the HNO_3–SO_3 system has shown[296] the existence of several compounds: $HNO_3,2SO_3$ is stable and melts at 106°C.; $HNO_3,3SO_3$ melts at 41°C. and a compound which may be $2HNO_3,3SO_3$ melts at 112°C. Further work[297] has shown that the compound $HNO_3,2SO_3$ contains the ions NO_2^+ and $HS_2O_7^-$; the compound $HNO_3,3SO_3$ is said to contain the ions NO_2^+ and $HS_3O_{10}^-$; the compound $2HNO_3,2SO_3$ is less stable than $HNO_3,2SO_3$. A phase diagram for the system nitrogen pentoxide–sulphur trioxide–water is given. Nine inorganic reactions in which nitric acid reacts to give the NO_2^+ ion are listed.

A patent[298] quotes recipes for preparing nitrating acids by absorbing sulphur trioxide in a liquid containing sulphur trioxide and nitrogen pentoxide in the molar ratio 1:4, to obtain nitryl pyrosulphate, $NO_2HS_2O_7$, which is then dissolved in nitric acid.

Liquid nitric acid and sulphur trioxide are almost completely miscible, but not between 90% and nearly 100% sulphur trioxide. A minimum in the vapour pressure diagram of the HNO_3–SO_3 system corresponds to the compound $HNO_3,2SO_3$. The vapour of mixtures on the nitric acid side of this minimum contains nitric acid and nitrogen pentoxide; on the sulphur trioxide side of the minimum it contains sulphur trioxide. Calorimetric measurements have been made[299] of the heats of mixing of various proportions of oleum containing 64·5% of free sulphur trioxide and anhydrous nitric acid (98·74%) plus sulphuric acid (1·26%). Heats of mixing of known proportions of nitric acid–sulphuric acid and liquid sulphur trioxide were calculated and hence the heats of formation of 1 g. of nitro-oleum from these three components. Further, from the heats of formation of nitro-oleums from the three pure components, the heats of reaction between sulphur trioxide and nitric acid were calculated. That for formation of $HNO_3,2SO_3$ was found to be 20·1 kcal./mole and to vary little with the excess of oleum from 9–40%; that for formation of $2HNO_3,3SO_3$ was found to be 15·0 kcal./mole. The curve of the heats of mixing of sulphur trioxide and nitric acid versus composition has a maximum at the composition $HNO_3,2SO_3$.

However, this work has been criticized by Russian investigators[300]; it is maintained that the maximum in the curve of heat of mixing versus composition corresponds not to $HNO_3,2SO_3$, but to $3HNO_3,4SO_3$, and its value is claimed to be 137 g.-cal. per g. of mixture instead of 64 g.-cal. as previously reported.

The absorption of gaseous sulphur trioxide by sulphuric–nitric acid mixtures has been examined.[301] The maximum concentration of sulphur trioxide in the acid mixture is approximately 9% at a concentration of sulphur trioxide in the gas of 7·5%. Under these conditions, however, the degree of absorption does not exceed 3%. In liquid containing nitric acid and sulphur trioxide in the molar ratio 1:0·5, spectroscopic evidence shows the presence of considerable amounts of nitronium, NO_2^+, and bisulphate ions.

Russian work,[302] in which the viscosity and density of nitric acid mixed with oleum of less than 45% w/w of sulphur trioxide were plotted against composition, has indicated that in the composition range in which $H_2S_2O_7:HNO_3=2:1$ the equilibrium:

$$2H_2S_2O_7+HNO_3 \rightleftharpoons NO_2HS_2O_7+2H_2SO_4 \qquad (a)$$

tends towards the right. Also, at *ca.* 25% nitric acid, the following reaction proceeds:

$$HNO_3+2H_2SO_4 \rightarrow H_3OHSO_4+NO_2HSO_4 \qquad (b)$$

In the composition range $H_2S_2O_7:HNO_3::1:1$, the reaction:

$$NO_2HS_2O_7+H_3OHSO_4+NO_2HSO_4 \rightarrow 2H_2NO_3HS_2O_7$$

is postulated, and is supported by the fact that the solution, on seeding with crystals of $H_2NO_3HS_2O_7$, crystallizes when slightly cooled. In the composition range $H_2SO_4:HNO_3=2:1$ the experimental results, taken in conjunction with spectroscopic evidence,[303] support the belief that the reaction occurring is:

$$NO_2HS_2O_7+HNO_3 \rightarrow 2NO_2HSO_4$$

Density data, plotted as a function of the nitric acid content of mixtures with oleum of less than 45% sulphur trioxide, gave curves with inflections corresponding to reactions (*a*) and (*b*) above; a third inflection was attributed to the reaction:

$$2H_2S_3O_{10}+HNO_3 \rightarrow NO_2HS_4O_{13}+2H_2SO_4$$

Mixtures of nitric acid with equimolar amounts of (i) sulphuric acid and of (ii) 44·9% oleum and (iii) a mixture with $HNO_3:SO_3::1:2$ have been studied[304]; in (i) and (ii), up to 200°C., the nitrogen is present essentially as nitronium ions (NO_2^+), but above 250°C., as nitrosyl ions (NO^+).

With Oxides of Nitrogen and Boron Trifluoride

The heat of solution of nitrogen dioxide in the system nitrogen dioxide–nitric acid, at 0°C., has been measured[305]; the data are discussed in relation to ionic reactions occurring in the system.

Crystalline nitrogen pentoxide is soluble in 100% nitric acid up to about 30% by weight. The minimum freezing point for the system is −69° at the composition $N_2O_5,6HNO_3$.[306] Cryoscopic study of mixtures of nitric acid with boron trifluoride[307] has shown the existence of $HNO_3,2BF_3$, m.p. 53°. Spectroscopic study of mixtures of nitric acid with 0·5, 1 and 2 molecules of boron trifluoride showed that in the first two cases the reaction:

$$HNO_3 + BF_3 \rightarrow NO_2^+ + BF_3OH^-$$

takes place to a considerable extent. In the last mixture, no clear evidence for the presence of NO_2^+ ions was found, the mixture probably being an addition compound.

With Acetic Acid

Viscosity and melting point measurements in the system nitric acid–acetic acid indicate the formation of a compound, presumed to be an addition compound.[308] This evidence is confirmed by Raman spectra[309]; the compound has the formula $CH_3CO_2H,HONO_2$.

When nitric acid is mixed with acetic anhydride, if the latter is in excess the products are acetic acid and acetyl nitrate; but if nitric acid is in large excess, nitrogen pentoxide is the main product.[310–312]

ORGANIC REACTIONS OF NITRIC ACID

Because of the importance and vast consumption of nitric acid in industrial organic chemistry, it is appropriate to include here a brief discussion of the behaviour of nitric acid towards the simpler and the industrially more important compounds of carbon. First, however, its effects on various forms of carbon itself are examined.

Carbon, Coal

The gas evolved when carbon is oxidized with nitric acid under specified conditions and in the absence of oxygen is rich in nitric oxide and free from nitrogen peroxide.[16, 313, 314] The reaction of coke with nitric acid is similar to that of coal, but the results vary with different cokes, even if they originated from the same coal. Blast furnace coke is more reactive than foundry coke, owing to the more amorphous nature, greater porosity and lesser hardness of the former and to the graphitic-crystal carbon in the latter.[315] The crystal structure of the compound of graphite with nitric acid has been studied.[316]

Oxidation of coal with nitric acid [317–330] or nitric acid and oxygen[331] leads to the formation of organic acids. The yields depend on (i) the kind of coal (ii) its petrographic constituents (iii) the physical and chemical pre-treatment (iv) its particle size (v) the concentration of the acid (vi) the catalyst (vii) the reaction temperature and (viii) the pressure. In one set of experiments the primary product contained aliphatic acids (4·4–11·5%), benzenedicarboxylic acids (4·7–9·0%), benzenetricarboxylic acids (13·9–21·0%), benzenetetracarboxylic acids (9·0–11·3%), benzenepentacarboxylic acids (3·4–9·4%), benzenehexacarboxylic acids (0·2%) and trinitrophenol (9·9–20·4%). The ether-insoluble material obtained from nitric acid oxidation of coal has been examined[332] and chromatographic separation of the constituents discussed.[333] The coal–nitric acid reaction may also serve as a source of phenol and carbohydrates and is claimed to be ten times as efficient as tar distillation. A useful review of this topic will repay study.[334] The effect of nitric acid on coal has helped to clarify the constitution of coal.[335] Treatment with nitric acid causes coal to lose its ion-exchange capacity[336]; however, when oxidizing catalysts are present, fuming nitric acid converts Assam coal,[337] for example, into an ion-exchanging material. Similar treatment of granulated lignite from the Landes basin followed by the passage of ammonia and air is said to give a product having good ion-exchange properties.[338] Organic acids, aromatic and aliphatic, can be produced by the oxidation not only of coal[317] but also of carbon black and pitch.[339] The use of salts of oxidation products of solid combustibles as surface active agents in bituminous paint or in insecticide dispersions has been claimed.[340]

Hydrocarbons

At elevated temperatures and at high pressures, methane may be oxidized in the vapour phase by nitric acid to give carbon monoxide and dioxide, water, formaldehyde and methyl alcohol; the formation of methyl alcohol is favoured by increased pressure, which apparently limits the chain-reaction leading to the simpler products.[341] A practical scheme has been presented for converting methane, from sewage digester gas, into formaldehyde using oxides of nitrogen from fuming nitric acid. [342] Ethane may be oxidized by nitric acid in the vapour phase at 455°C. and 100 lb./sq. in., giving nitroethane and nitromethane.[343, 344] The catalyzed oxidation of methane, ethane and propane by air in the presence of nitric acid, to give formaldehyde, has been patented.[345] Similarly, but without catalysts, these and higher paraffinic hydrocarbons may be converted to nitroalkanes and formaldehyde.[346] Long-chain hydrocarbons may be oxidized under pressure and at elevated temperatures to the corresponding β-substituted mono-nitroalkanes; hydrocarbons with more than a critical number of carbon atoms yield disubstituted (β, β'-) compounds.[347] The formation of C_6–C_{12} dicarboxylic acids from paraffins has been examined.[348] The reaction mechanism of the nitration of hydrocarbons has been extensively studied; the ineffectiveness of nitric acid at room temperatures is contrasted with its effects at temperatures above about 300°C.; it is concluded that nitrogen dioxide is the active species.[349–351] The action of nitric acid on mercury-paraffin compounds has been studied in connection with the action of the acid on the paraffins themselves.[352] Nitric acid, from the nitrous gases formed in the cylinders, quickly causes deterioration in internal combustion engine oils.[353] The reactions between nitric acid and the liquid hydrocarbons are of particular importance in rocketry (see p. 341).

Ethylene reacts with fuming nitric acid to give carbon dioxide, oxalic acid, α-nitro-β-hydroxyethane and tetranitromethane. Mercury salts encourage the production of carbon dioxide at the expense of the other products. Equations have been derived for the probable course of the reaction.[354]

Acetylene is readily absorbed by concentrated nitric acid, or a mixture of this with sulphuric acid; absorption is accelerated by increased temperature and by the addition of mercury salts. Tetranitromethane may be obtained from the reaction products by treatment with sulphuric acid; trinitromethane and oxalic acid have been identified among the products.[355] Quilico and Freri have published a series of papers on the effect of nitric acid on acetylene and have identified many of the reaction products.[356–362]

The action of nitric acid on the alicyclic hydrocarbons has a vast literature; the subject is not discussed here, but references to the more important, commercially-used reactions will be found under 'Applications of Nitric Acid'.

It has been reported that aryl–silicon bonds may be broken by nitric acid; aromatic nitro-derivatives are formed which carry NO_2 groups in the positions formerly occupied by silicon.[363, 364]

Alcohols

Nitric acid reacts with simple alcohols as an acid to give organic nitrates and as an oxidizing agent to give various oxidation products. Thus, in the presence of ethyl lactate, methyl alcohol may be converted into methyl nitrate.[365] The susceptibility of the primary alcohols to oxidation increases with the length of the chain; thus ethanol is oxidized more readily than methanol, and secondary alcohols are more susceptible than primary alcohols.[366] In the presence of cupric nitrate or nickel (II) nitrate, ethanol reacts with nitric acid to give oxalic acid.[367] Propanol gives the same product.[368]

Large tonnages of nitric acid are used in the explosives industry for 'nitrating' polyhydric alcohols, particularly glycerol and cellulose, to produce nitrates which, in this context, are commonly named nitro-compounds, and a review of this use has been published.[369] This subject is discussed more fully under 'Applications of Nitric Acid'.

A laboratory investigation into the factors influencing yields and safety in the manufacture of nitrates of glycols has been reported and optimum nitration conditions described for glycol, diethylene glycol, triethylene glycol and 1,3-butanediol as well as glycerol.[370] The equilibrium between mononitroglycol and dinitroglycol:

$$\mathrm{MNG}+\mathrm{HNO_3} \rightleftharpoons \mathrm{DNG}+\mathrm{H_2O}$$

has been studied at an initial nitric acid concentration of 10–11%. The equilibrium constant increases from 1·96 to 4·21 with increasing water concentration, this being attributed to the formation of a compound by addition of nitric acid to the ether oxygen atom of mononitroglycol. In the nitration of diethylene glycol, the equilibrium constant decreases with increasing water concentration and this is attributed to increasing dissociation of the nitric acid. Hydrogen ions catalyze the denitration of both mono- and dinitro-glycol and this reaction is much more rapid than is that with nitroglycerol.[371]

Penta-erythritol may be nitrated to give a powerful explosive.[372]

The preparation of adipic acid, an intermediate in the manufacture of nylon, is an example of the oxidation of an alcohol (*cyclo*hexanol) by nitric acid; copper and ammonium vanadates are used as catalysts. The optimum acid concentration is 40–50%, for weaker acid leads to increased yields of glutaric and succinic acid; in the absence of a catalyst the yields of succinic and oxalic acids increase.[373–377]

Cellulose

Cellulose reacts with nitric acid to give predominantly hydrolysis products if the acid is weak or nitro-derivatives if the acid is strong. Using acid of less than 70% concentration, only the cellulosic hydroxyl groups are the points of uptake for the NO_2-OH molecules and probably only one per glucose unit. The reacting substance is probably nitric acid monohydrate:

$$\mathrm{NO_2.OH.OH_2}+\text{cellulose–OH} \rightarrow \mathrm{NO_2}\text{–OHHO–cellulose}+\mathrm{H_2O}$$

The equilibrium occurs throughout mercerized cellulose fibre, but only partially in native cotton.[378] Addition of oxides of nitrogen to the nitric acid, in the absence of sulphuric acid, causes a higher degree of nitration and by using a mixture of 95% nitric acid and 5% nitrogen pentoxide, a nitrocellulose containing 13·7–13·8% of nitrogen can be obtained. 96% Nitric acid alone gives a product containing 13·0% of nitrogen.[379] Nitric acid which is 'immobilized', as complexes with water or salts, has no nitrating effect; the latter is directly proportional to the concentration of 'free' nitric acid.[380–384] A review of some industrial aspects of cellulose nitration has been made.[385] Cotton may be mercerized by nitric acid alone[386–389] or by nitric acid prior to treatment with sodium hydroxide.[390] As part of a study of nitric acid processes used in the manufacture of pulp, surgical cotton (α-cellulose, 98·7%; copper number, 0·01) was treated with (i) 40% nitric acid at 14°C. for 3–12 hours (ii) 5% nitric acid at 100°C. for 2 hours (iii) 20% nitric acid at 80°C. for 1 hour, followed in each case by soaking for 4 hours in 1% sodium hydroxide at 20°C. (i) led to no change in α-cellulose content or copper number; (ii) led to a decrease in α-cellulose content to 91·5% and an increase in copper number to 2·10; (iii) led to a decrease in α-cellulose content to 87·2% and an increase in copper number to 2·79. When applied to straw, treatment (i) gave the highest yield (51%) and the strongest pulp.[391, 392] Cellulose pulp may be separated from many vegetable products after the non-cellulosic constituents have been oxidized with nitric acid. In the process of the Dresden Textile Research Institute, a 3–5% nitric acid solution suffices to resolve the raw materials into fibres after a digestion period of 6–8 hours at 95–96°C. After acid removal, washing and neutralizing with lime and sodium carbonate, the mass is easily broken into its fibrous constituents.[393, 394] A Hungarian process starting from straw, a Japanese one from bagasse and a Spanish one from straw have also been described.[395, 396, 397]

Wood is another source of raw cellulose. When treated with nitric acid the degree of degradation increases with the time of cooking, with increase of acid concentration and with increasing temperature, the last being the most important factor. The addition of nitrates, especially chromium nitrate, causes an increase in the rate of acid attack.[398] A substantial quantity of furfuraldehyde is produced from unremoved pentosans when wood pulp is made by the nitric acid route. The nitric acid may be partly replaced by sulphuric acid.[400] Various kinds of wood may be used[401–409] and several reviews of the subject have been published.[410, 411, 412]

The effect of nitric acid on the wet strength of paper[413] is thought to result from the formation of hydrogen bonds between adjacent cellulose chain molecules.[414]

Miscellaneous

Nitric acid reacts with glycine to give the addition products HNO_3,Gl and HNO_3,2Gl.[415] Oxidation of cystine with nitric acid alone gives incomplete conversion of its sulphur to sulphate,[416] but the yield is increased by the presence of substances capable of reducing the acid to oxides of nitrogen.[415] The amount of acid which combines with wool depends on the pH of the solution, amongst other factors, and the subject has been reviewed.[417]

Other organic materials which react with nitric acid may be mentioned here. Oxalic acid may be oxidized by nitric acid and the reaction kinetics have been studied.[418] Ether reacts violently with absolute nitric acid at room temperature, there being a marked induction period owing to autocatalysis by oxides of nitrogen. There is an even more violent reaction between nitric acid and ether when sulphuric acid is present.[419] A mixture of equal volumes of acetone, concentrated nitric and 75% acetic acid, used for etching nickel, is liable to explode spontaneously a few hours after the mixture has been made up.[420]

MISCELLANEOUS REACTIONS OF NITRIC ACID

Isotopic exchange reactions between nitric acid and various related substances have been examined; in a 40% solution, the acid undergoes oxygen exchange with water, with a half-life of *ca.* 30 minutes at 30°C.[421] The reaction:

$$^{15}NO(g) + H^{14}NO_3(aq.) \rightarrow {}^{14}NO(g) + H^{15}NO_3(aq.)$$

is favourable for the separation of nitrogen-15. The presence of nitrogen dioxide, nitrogen trioxide and nitrous acid in the liquid phase apparently accelerates the exchange.[422, 423] Tritium as a tracer has been used to show that the exchange rate between ammonium nitrate and 54% nitric acid has a half-life of *ca.* 3 minutes.[424]

In the thermal decomposition of nitric acid vapour at 400°C. optical analysis has shown that the fast initial rate is inhibited by nitrogen dioxide, unaffected by water vapour and oxygen and sustained by nitric oxide.[425] In the presence of excess of reducing agents, e.g., hydrogen, carbon monoxide, or methane, the decomposition rate was first-order with respect to nitric acid, independent of reducing agent concentration and of the same order of magnitude as the initial decomposition rate of nitric acid vapour alone. Results were in accord with the mechanism:

$$HNO_3 \rightarrow HO + NO_2;\ HO + HNO_2 \rightarrow H_2O + NO_3$$
$$NO_2 + NO_3(\equiv N_2O_5) \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$

The velocity of absorption of oxygen in the system nitric acid–nitrogen dioxide–water has been shown to fall rapidly at 63% strength acid, becoming nearly zero in 79% acid.[426] The solubility of oxygen in white and in red fuming acid has been found to pass through a minimum, when plotted as a function either of the water or of the dinitrogen tetroxide present, at 80–85% w/w acid.[427] The solubility of oxygen in pure nitric acid and in the mixtures $0{\cdot}94HNO_3+0{\cdot}06H_2O$ and $0{\cdot}85HNO_3+0{\cdot}15NO_2$ increases with temperature in the range 37–90°C.[428] Nitric acid has been predicted to be among the prevalent nitrogen compounds in urban air[429, 430] and the photochemical processes in which it probably participates in connection with smog formation have been reviewed.[431]

Nitric Acid as Non-aqueous Solvent

Reactions using absolute nitric acid as a non-aqueous solvent (e.g., potassium nitrate with perchloric acid) have been examined. Pure anhydrous nitric acid dissolves inorganic and some organic compounds to give solutions which are generally good conductors of electricity. Although the alkaline earth nitrates are nearly insoluble, silver nitrate dissolves to the extent of 0·2 g. in 100 g. of acid and the alkali metal nitrates are very soluble, as also is tetramethylammonium nitrate. Other substances which dissolve are mostly in their most highly oxidized states, e.g., perchloric and phosphoric acids, water and chromium trioxide.[432] Solvolysis and amphoteric reactions are reported.[433] With silicon tetrachloride a stepwise reaction resulting in the formation of silicic acid occurs. The jelly product, having the composition $3SiO_2{,}2H_2O{,}xHNO_3$, is apparently as good an adsorbent as ordinary silicic acid jelly. Cooled mixtures of absolute nitric acid with excess of titanium tetrachloride yield deep yellow $TiOCl(NO_3)$ which with further nitric acid gives a white precipitate containing 20% TiO_2 and 80% HNO_3. Stannic and pentavalent antimony chlorides likewise give an intermediate solvolysis product followed by a solvated jelly of stannic acid or an adsorption compound of antimony pentoxide with nitric acid, respectively. Phosphorus oxychloride gives first phosphorus oxynitrate, $PO(NO_3)_3$, followed by metaphosphoric acid. Uranyl nitrate is amphoteric in nitric acid and reacts on the one hand with perchloric acid and on the other with potassium nitrate or tetramethylammonium nitrate. Cadmium nitrate shows less marked amphoteric character. Hexamminechromium (III) nitrate and hexamminecobalt (III) nitrate are fairly soluble in absolute nitric acid without decomposition. The conductivity of the solutions increases with the concentration, i.e., both salts are extensively electrolytically dissociated.[434]

In certain non-aqueous solvents, nitric acid may be titrated with bases; thus in pyridine and in dimethylformamide its titration against tetrabutylammonium hydroxide can be followed potentiometrically.[435] In a solvent mixture of ethylene glycol, butanol and benzene, nitric acid may be titrated against sodium hydroxide.[436]

Effect of Nitric Acid on Solubility of Nitrates

The influence of nitric acid on the solubility of nitrates in water results in a minimum in the solubility versus temperature curve; thus for silver, copper, potassium, sodium and ammonium nitrates, the minimum lies in the region between 0° and 30°C.; copper, potassium and sodium nitrates also show a minimum but at 75°C. The minimum is most pronounced with salts capable of forming acid salts. The lowering of solubility by nitric acid is an exponential function of its concentration.[437] If aqueous nitric acid is treated as a binary solvent containing x mole fractions of nitric acid itself and $(100-x)$ mole fractions of water, then the solubility L of a nitrate is given by:

$$L = l_1+l_2 = L_1(1-0{\cdot}01x)^{n_1}+L_2(0{\cdot}01x)^{n_2}$$

where l_1 and l_2 are the partial solubilities of the nitrate in water and in pure acid, and L_1 and L_2 are the solubilities of the nitrate in water and in the pure acid, respectively. From experimental data sufficient for setting up only two equations, and by making certain simplifying assumptions, values of n_1 and n_2 can be obtained. This procedure has been successfully carried out for potassium nitrate as to its solubility in aqueous nitric acid.[438] General[439] and specific[440–442] studies have been made of nitrate solubility in nitric acid.

Effect of Nitric Acid on Distribution Coefficient of Nitrates

The effect of nitric acid on the distribution coefficient of the nitrates of lanthanide and uranide elements between aqueous and non-aqueous phases is of great practical importance in the atomic energy field; much detailed information is still classified as secret. In the presence of nitric acid and/or ammonium nitrate these elements form complexes in the non-aqueous phase. Thus with only nitric acid added to an approximately 1·5 M. solution of uranyl nitrate the partition coefficient for the latter between the aqueous phase and diethyl ether reaches a maximum of 2·35 when the former phase is 4·7 M. in nitric acid. With the same uranyl nitrate solution saturated with ammonium nitrate, and in the absence of nitric acid, the partition coefficient reaches a maximum value of 3·7. The corresponding value for a simple uranyl nitrate solution is only 0·08 at 20°C. In the extraction of small or moderate amounts of uranyl nitrate with ether from aqueous solution it is advantageous to saturate with ammonium nitrate, while the aqueous phase is maintained at 1–2 M. with nitric acid.[443, 444]

A general study has been made of the solvent extraction of uranyl nitrate, aided by nitric acid.[445] Electrophoresis data have shown that in the presence of nitric acid, uranyl nitrate enters a cationic complex at all concentrations.[446] Similar effects are observed in tributyl phosphate extractions.[447] A study has been made of the complexes of this solvent with several inorganic nitrates.[448] The effect of increasing nitric acid concentrations in solutions of rare earth tracers on their distribution ratios with tributyl phosphate divides these elements into three groups: (*a*) the distribution ratio for the lighter rare earths increases rapidly up to 1·5 M. acid and then steadily decreases; (*b*) the distribution ratios for the heavier rare earths increases up to 3·0 M. acid and then continues to increase at a lower rate; and (*c*) the ratios in the middle group increase rapidly up to 1·0 M. acid and remain constant until about 5 M. acid is reached.[449] In the tributyl phosphate–water–nitric acid system the existence of a compound HNO_3,TBP has been demonstrated.[450] The use of nitric acid to aid the solvent extraction of cerium,[451] thorium,[452] polonium,[453] actininium[454] and neptunium[455] has been reported.

In ion-exchange separations of uranium on cellulose columns, a mixture of petroleum ether, diethyl ether and nitric acid may be used.[456] In the separation of zirconium and hafnium by cation exchange on Dowex-50 resin, a mixture of citric and nitric acids has been found most effective.[457]

The effect of nitric acid on the time of gelation of sodium silicate is similar to that of other common acids.[458, 459] If alumina gel of high specific surface area is treated with nitric, hydrochloric or sulphuric acid, the surface area is reduced, the *X*-ray diffraction pattern is changed and anions are introduced.[460] The rate of neutralization of nitric and other acids by hydrous alumina has been examined.[461] The coagulation value of nitric acid on negative silver bromide sol has been measured[462] and the effect of nitric acid on the formation of barium sulphate suspensions has been reported.[463] The solubility of cupric oxide[464] and of niobium hydroxide,[465] and the heat of solution of several praseodymium oxides,[466] in nitric acid have been recorded.

Addition of 50% aqueous nitric acid as a spray to calcium cyanamide to give a nitrogeous fertilizer containing nitrate, urea and dicyandiamide has been patented.[467] Iron carbide reacts with nitric acid (*d* 1·17) to give, after purification, a blackish powder insoluble in organic solvents, but soluble in alkali. It is reprecipitated from the latter by addition of acid or a salt of a non-alkali metal. It has an elemental analysis of C 56·3, H 3·3, N 3·8, O 37·7% w/w. If nitric acid (*d* 1·33) is used for reprecipitation, a similar product having the slightly different composition C 59·2, H 2·8, N 3·6, O 34·4% w/w results. These products bear resemblance to the humic substances extracted from humus.[468, 469] The colour reaction produced by the action of nitric acid on iron carbide has been attributed to reaction between nitrogen peroxide and the olefines produced by the acid attack.[470]

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APPLICATIONS OF NITRIC ACID

Although nitric acid was prepared by oxidation of ammonia with air, using a heated platinum catalyst, as early as 1839, large-scale commercial production by this means did not begin until 1909, in Germany, and not until 1916 in the United States. Production since then has steadily increased, most markedly in the years following 1941.[471–473] (See Table I.)

Table I.—Annual Nitric Acid Production in U.S.A. and U.K. (*tons* × 10^{-3})

	Year						
	1931	1933	1935	1937	1939	1941	1942
U.S.A. production	106·3	86·7	87·2	159·6	152·1	314·8	388·0
U.K. production	—	—	—	—	—	258·6	355·0

	Year						
	1943	1944	1945	1946	1947	1948	1949
U.S.A. production	438·3	427·9	405·6	520·5	1079·0	1027·7	1024·7
U.K. production	386·8	347·2	285·5	232·4	203·0	244·0	244·6

	Year							
	1950	1951	1952	1953	1954	1955	1956	1957
U.S.A. production	1211·7	1372	1479	1601	1812	2091	2352	2559
U.K. production	257·6	281	308	308	—	—	—	—

The manner in which nitric acid is consumed in peace-time has been estimated[474] as: ammonium nitrate fertilizers, 55%; explosives, 25%; miscellaneous 20%. A more detailed classification is shown in Table II. A general discussion of the applications of the acid has been given.[475]

Table II.—Uses of Nitric Acid

Classification	Examples
Production of Nitrates (dilute or concentrated acid)	Ammonium nitrate Compound fertilizers Barium and strontium nitrate Cellulose nitrate Nitroglycerol
Production of Nitro-Compounds (concentrated acid)	Explosives (e.g. T.N.T., picric acid) Dyestuffs intermediates Weedkillers (e.g. dinitro-*o*-cresol) Insecticides (e.g. nitrostyrene) Fungicides (e.g. dinitrophenol) Nitroparaffins
Oxidising Action (usually dilute acid)	Rocket propellants Benzoic acid from toluene Iodic acid from iodine Arsenates from arsenites Ferric salts from ferrous salts
Action on Metals (usually dilute acid)	Pickling light alloy castings Etching and photogravure Refining precious metals

Ammonium nitrate is manufactured in very large quantities both for fertilizer and for explosive uses; for details of its chemistry and applications see Vol. VIII, Suppl. 1, p. 506.

In the production of compound fertilizers, nitric acid can play a part not only as ammonium nitrate, but also as a substitute for sulphuric acid in treating phosphate rock (see 'Acid Properties'). Four major development possibilities for nitric acid are visualized in a review by Crittenden[476]; (1) continued expansion of ammonium nitrate products; (2) ultimate production of potassium nitrate as a fertilizer; (3) expansion of calcium nitrate production, and (4) growth of phosphate rock processing. In this last use of nitric acid, the extent to which it is found economic depends (*a*) very much on the availability and cost of the sulphur used to make sulphuric acid, which may be replaced by nitric acid in phosphate rock processing, and (*b*) on the availability and form of fixed nitrogen, this latter particularly affecting transport costs.

Barium nitrate is made from nitric acid and barium carbonate; it may also be made by dissolving sodium nitrate in a saturated solution of barium chloride, when barium nitrate is precipitated. Thus for example *ca.* 11,000 tons were made in U.S. in 1944. It is used in fireworks, flares, tracer bullets, detonators, primers and, in enamels, as a source of barium oxide.[477]

Strontium nitrate is made (*a*) by treating strontianite, the chief carbonate mineral, with nitric acid, or (*b*) by digesting celestite, the sulphate mineral, with soda ash followed by treatment with nitric acid. Recrystallization yields high-purity anhydrous nitrate. Its main use is in fireworks (crimson colour) and in railway warning flares; it may also be used in tracer bullets.[478]

Nitroglycerol

Large tonnages of nitric acid are used in explosives manufacture for nitrating polyhydric alcohols (e.g., glycerol, cellulose) and hydrocarbons (e.g., toluene). Nitroglycerol is made by adding anhydrous glycerol to a stirred mixture of nitric and sulphuric acids, the latter helping to remove the water liberated in the reaction and promoting the formation of the fully esterified product.[479–486] Nitroglycerol detonates violently on slight shock with the liberation of a large volume of gas (chiefly nitrogen, carbon dioxide and water) and this sensitivity made the early production of nitroglycerol hazardous. Modern production processes operate under very strictly controlled conditions and have greatly reduced the danger of accidental explosions. The original Nobel plant operated a batch process, using open porcelain or enamelled cast-iron pots as reaction vessels. Glycerol was added slowly to the mixed acids which were stirred with a glass rod by the operator. No cooling was provided, so that the charge was kept down to one or two pounds of glycerol per vessel. In spite of this, the plant was destroyed after operating for two years. The batch process has now been developed to a high state of efficiency, using cooled vessels with their contents stirred by mechanical or air agitation systems. By controlling such factors as acid composition, temperature and the washing technique for the product, the yield can be as high as 96% of the theoretical. A process for continuous nitration was patented as early as 1878, but no acceptable process was evolved until Schmid's in 1927 and one by Biazzi later. The former process has been used in Europe, but not in America.

Recent Biazzi process[487] plants have been considered so free from hazard that it was judged unnecessary to duplicate equipment in case of loss. A schematic diagram of the process is given in Fig. 2.

Glycerol, ethylene glycol and the mixed acids are stored in separate tanks outside the main plant and are pumped at controlled rates to the nitrating house. The nitrating equipment is constructed of stainless steel with highly polished interior surfaces which cannot trap nitroglycerol. It is fitted with internal cooling coils, through which cold brine is passed. Acid enters the nitrator through a single open pipe and reacts with the mixture of glycerol and glycol, which is supplied as a

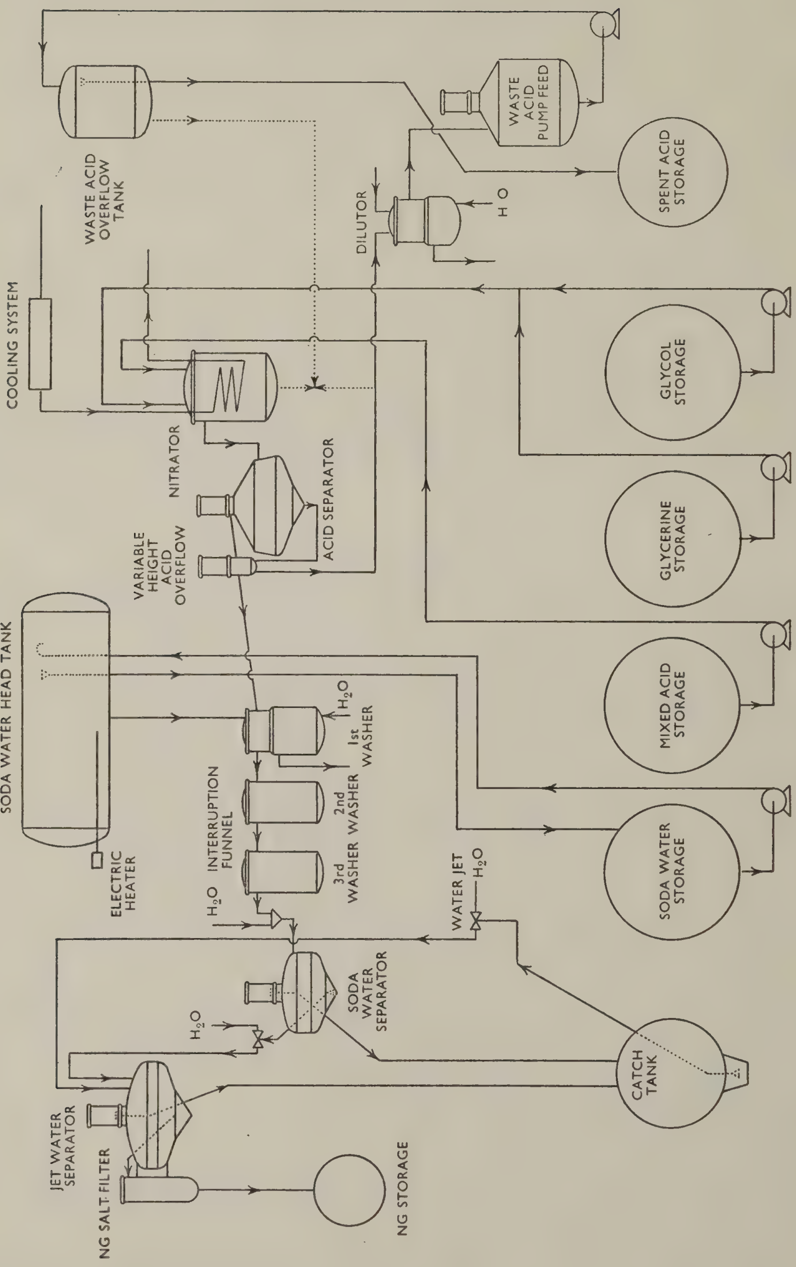

Fig. 2.—Schematic diagram of Biazzi process plant

number of fine streams. The mixture is agitated by an impeller-type stirrer, the motor for which is housed outside and which incorporates a flywheel to prevent sudden changes in speed. Under the action of the impeller the liquids are drawn towards the bottom of the vessel and are then thrown outward by centrifugal force towards the walls. Rapid reaction ensues and the emulsion of nitroglycerol in spent acid rises. Part leaves the system by an overflow pipe and part is drawn to the centre and down again. There are no valves in the path of the nitroglycerol, which flows freely under gravity from nitrator to the washing vessels and to storage. In case of emergency, the mixture in the nitrator can be dumped into water by opening a flap valve. The Biazzi nitrator is claimed to have a number of advantages when compared with the batch process:

(i) Agitation is more efficient and this avoids local overheating and oxidation of glycerol.

(ii) Heat transfer between the reactants and the cooling medium is better because of the higher ratio of cooling surface to volume. Hence the cooling brine can enter at a higher temperature, which in turn reduces the danger of nitroglycerol (m.p. 13°C.) freezing on the coils. Frozen nitroglycerol is much more sensitive to initiation by friction than is the liquid. The danger of freezing is also reduced by the use of ethylene glycol in the mixture; a mixture of equal volumes of nitroglycol and nitroglycerol freezes at about −60°C.

(iii) There is a nearer approach to countercurrent cooling owing to the regular flow of reactants along the cooling coils.

(iv) There is a smaller quantity of nitroglycerol in the process at a given time; a plant can be shut down and cleared of nitroglycerol in about 15 minutes.

The emulsion of nitroglycerol in acid passes to an empty separating vessel (the corresponding vessel in the Schmid process contains baffle plates); it enters tangentially and the rotation so imparted aids separation of the nitroglycerol. Nitroglycerol is removed from the top of the separator and spent acid from its bottom and side. The vessel has a drowning system similar to that of the nitrator. Nitroglycerol leaving the separator still contains some 6% of nitric acid and 0·3% of sulphuric acid and these must be removed to give a stable product. It is therefore washed in three stainless steel vessels fitted with agitators of the nitrator pattern. In the first washer it is mixed with an equal volume of 13% sodium carbonate solution and the heat of reaction is removed by cooling water in a jacket, so that the emulsion temperature does not exceed 95°F. Gas is taken off through a suitable outlet. The second and third washers are similar, but without cooling or soda inlet. They ensure complete neutralization.

A detailed study has been made of the various equilibria involved in the washing of nitroglycerol.[488] The presence of oily trace impurities in nitric acid made from sodium nitrate and sulphuric acid, e.g., $C(NO_2)_4$, $CCl(NO_2)_3$, $CCl_2(NO_2)_2$, has given rise to difficulties in the washing of nitroglycerol. Their formation is probably due to the chlorides and organic matter in the sodium nitrate used in this outmoded method of nitric acid manufacture.[489]

The neutralized nitroglycerol passes from the third washer to the separation building, an interruption funnel being installed to provide a break in the film of nitroglycerol in the line. It passes through two separators in series and thence to storage tanks.

It has been shown that liquid nitric esters of glycerol, glycol and similar sensitive compounds can be safely piped over distances up to 300 ft. through a large number of small bore pipes ($<0{\cdot}1$ inch internal diameter) under pressures of up to twenty times the normal pressure.[490] The spent acid contains (in suspension) less than half a pound of nitroglycerol per ton together with a further quantity in solution, the amount of the latter depending markedly on the spent acid composition. Water is added to prevent separation of the emulsion, and weak nitric acid (60%) and sulphuric acid (70%) are recovered.

Spent wash water can be extracted with a non-explosive aromatic hydrocarbon, e.g., *o*-nitrotoluene, to extract the residual explosive esters and to permit the safe disposal of the wash water.[491]

Trinitrotoluene, T.N.T.

2:4:6-Trinitrotoluene, T.N.T., is perhaps the most important modern high explosive; first prepared on an industrial scale in 1891 in Germany, by 1901 it began to displace picric acid and was adopted by the military authorities. Solid T.N.T. is relatively insensitive to shock, and is one of the most stable bursting-charge explosives; even at 150°C., little decomposition is observed after 40 hours. Molten T.N.T. is much more shock-sensitive than solid T.N.T., the former being comparable to mercury fulminate. It is only moderately toxic, and is non-vesicant and non-lachrymatory. It freezes at 80·75°C., and is soluble in water only to the extent of 13 mg./100 ml. at 20°C. Having all these properties T.N.T. has, not surprisingly, become a very popular explosive.

It is usually manufactured by a three-stage process, by which one nitro-group at a time is introduced into the molecule. Compared to one or two-stage processes, the three-stage process affords greater yield, purity and ease of control. Typical compositions for the three acid mixtures used in these stages are shown in Table III below.

Table III.—Approximate, Typical Compositions of Acid Mixtures used in Three-stage Process for making T.N.T.

Components of acid mixture	Stage 1 % w/w	Stage 2 % w/w	Stage 3 % w/w
Sulphuric acid	48	54	82·7 (total equivalent H_2SO_4)
Nitric acid	14	13	23·3
Nitrosyl sulphuric acid	17	17	—
Water	19	8	—
Organic material	2	8	—

The rates of rise of temperature and the maximum temperatures reached are very carefully controlled. After each nitration stage, the spent acid is allowed to settle and is drained off. Spent acid from the third stage is fortified and used for the second stage nitration; spent acid from the second stage is similarly fortified and re-used. The nitrated oil made at each stage is pumped to intermediate tanks before it is passed to the next stage. The control of the third stage is particularly critical in determining the amounts of unreacted dinitrotoluene remaining in the crude T.N.T.; normally the chief impurities are 2:3:4- and 3:4:6-T.N.T., accompanied by oxidation and nitration products such as tribenzoic acid, trinitrobenzene and tetranitromethane, making in all 5–7% of total impurities.

The crude T.N.T. is washed with hot water, to remove free acid, and then crystallized; alkali is added to neutralize the last traces of acid, care being taken to avoid excess of alkali which would tend to decompose the T.N.T. A buffered sodium sulphite solution is then added; it reacts with the unwanted T.N.T. isomers to give the sodium salts of the corresponding dinitrotoluenesulphonic acids, the aqueous phase becoming red owing to the formation of some hexanitrobibenzyl from 2:4:6-T.N.T. Tetranitromethane is converted to sodium trinitromethanesulphonate and sodium nitrate. The soluble impurities are removed by washing with water, and the unaffected dinitrotoluene tends to be carried away mechanically. The washed T.N.T. is melted, again washed with hot water, dried by air agitation at or above 100°C. and is cooled, flaked and grained.[492]

Further information on the manufacture of high explosives, in which so much nitric acid is used, is available.[493, 494]

Another important explosive made from nitric acid is RDX, *cyclo*trimethylenetrinitramine. Its formation from hexamine, from hexamine mononitrate and from hexamine dinitrate have been studied.[495, 496, 497] It can also be made from ammonium nitrate and formaldehyde in glacial acetic acid, nitric acid being formed *in situ*.[498]

Rocket Propellants

Nitric acid is also used in rocketry. Much attention has recently been devoted to the development of rocket motors and fuels, and for this purpose nitric acid is one of the favoured oxidizing agents. The fuel may be ammonia, hydrazine, boron hydride or any of a variety of organic compounds.[499–510] The most efficient propellant is that giving the greatest volume of gas per unit weight, so that high temperatures and breakdown to smaller molecules are desirable. Similarly, as the partially burned products, carbon monoxide and hydrogen, have lower molecular weights than the products of complete combustion, carbon dioxide and water, a mixture slightly on the fuel-rich side of the stoicheiometric ratio for complete combustion may be preferred. Although nitric acid contains a lower weight-% of oxygen than does liquid oxygen, it has greater stability. Corrosion by nitric acid is a serious problem, somewhat offset by the addition of 10% of sulphuric acid[511] and the use of nitric acid also creates problems in welding and sealing.[499] Compared to a system using gasoline and liquid oxygen, the systems using red fuming nitric acid are about 10% lower in specific impulse, but the 40% greater density of the acid more than counters this disadvantage. Bi-propellant systems such as gasoline–nitric acid are non-self-igniting (non-hypergolic) but can be rendered self-igniting by the addition of 15–25% or more of a terpene hydrocarbon.[512] Mixtures of fuming nitric acid with aniline or furfuryl alcohol are self-igniting. Much attention has been paid to the speed with which self-ignition occurs in the mixture of fuel and oxidizing agent.[513–524] The disadvantageously high freezing point of fuming nitric acid and the relatively long ignition delay in its reaction with mixed mercaptans have been improved by adding an alkanesulphonic acid containing between one and five carbon atoms.[525] The ignition delay has been considered to depend partly on the chemical nature of the feed and partly on its physical characteristics.[526] Thus the addition of 0·5% of a surface active agent has been found to decrease considerably the time for self-ignition.[516] Studies have been made of the burning rate of single fuel droplets falling through the vapours of white fuming nitric acid.[527, 528] Current bipropellant systems give a specific impulse of 200–225 sec., with flame temperatures of 2000–3000°K., but as it is not generally possible to use chamber temperatures above 2500°K. the higher specific impulses are not yet attainable.

Of the three chief oxygen carriers, liquid oxygen, hydrogen peroxide and nitric acid, the last has the smallest specific volumetric consumption and this affects propellant loading as well as aeronautical and ballistic application of the rocket power plant.[529, 530]

Miscellaneous

Another oxidative use of nitric acid is in the preparation of organic acids from sugars; thus xylose yields tri-hydroxyglutaric acid[531–533]; dextrose yields saccharic acid[534]; glucose yields tartaric acid or saccharic acid[535, 536]; *D*-galactose gives mucic acid[537]; the oxidation of lignite gives oxalic acid among other products.[538] The oxidation of coal by nitric acid is discussed under ‘Organic Reactions’.

The use of nitric acid for pickling metals in order to provide a clean surface prior to deposition of a coating of metal or other substance has been described. Particular examples are aluminium,[539, 540] steel[541–547] and titanium.[548] Related suggested

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uses are in pickling zirconium machining chips followed by recovery of the decontaminated metal,[549] processing of aluminium and magnesium powders by removing surface impurities with concentrated nitric acid,[550] and increasing the surface area of kieselguhr.[551] Direct chemical polishing of metals is also possible and is described for aluminium,[552–555] brass and German silver,[556] germanium,[557] magnesium and its alloys[558, 559] and a low carbon steel.[560] Acids other than nitric are normally incorporated in such baths. The replacement of sulphuric acid by nitric acid in mixtures with potassium dichromate used for cleaning glass has been advocated.[561]

Other applications of nitric acid are legion; thus, it can be used in producing paper from wood (pulping) (see 'Organic Reactions); for removing carbonaceous impurities from sulphuric acid[562]; for increasing the absorption efficiency of oleum for sulphur trioxide[563] (see also 'Addition Compounds'); for purifying sulphonic acids[564]; for recovering boric acid from borates[565]; for extracting magnesia from serpentine,[566] iodine from seaweed[567] and nickel from neponite[568]; for destroying the organic flotation agents used in the production of titanium oxide[569]; and for cleaning apparatus, e.g., brewery vats.[570] The hydrolysis products of cork may be oxidized by nitric acid to yield waxy materials.[571] Finally, nitric acid may even be used for treating warts.[572]

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SECTION XXXII

NITROUS ACID, HYPONITROUS ACID AND THEIR SALTS

BY H. BLOCK

NITROUS ACID

Formation

Nitrous acid is formed by the action of ultrasonic radiation on water containing dissolved air.[1–7] Prolonged irradiation results in a decrease in the nitrous acid concentration owing to nitric acid formation. The oxidation of nitrogen under these conditions has been found[4] to decrease with increasing temperature in the range 10–50°C. and to cease[6] above 67°C. Ultrasonic radiation also catalyzes the decomposition of nitrous acid.[8] Nitrous acid has been found[9] as a condensable product when ammonia and oxygen mixtures are passed over a heated platinum wire catalyst; investigation[9] has elucidated the steps of the free-radical mechanism involved. A similar oxidation of ammonia and of hydroxylamine occurs under the influence of *X*-rays[10] when these substrates are in dilute aqueous solution. Hydroxylamine is oxidized 5×10^3 times faster than ammonia. The hydrolysis of nitrosyl chloride results in the formation of nitrous acid by means of the equilibrium:

$$NOCl\ (aqueous) + H_2O\ (liquid) \rightleftharpoons HNO_2\ (aqueous) + HCl\ (aqueous)$$

for which the thermodynamic equilibrium constant has been determined to be[11] $(8{\cdot}8 \pm 0{\cdot}4) \times 10^2$ or[12] $(9{\cdot}0 \pm 0{\cdot}3) \times 10^2$ at 25°C. The free energy change for this reaction is reported[11] as $-4{\cdot}019$ kcal./mole at 25°C.

The reaction of dinitrogen tetroxide with water (Mellor, VIII, 455) has received much attention, mainly with a view to the formation of nitric acid. The primary reaction:

$$N_2O_4 + H_2O \rightleftharpoons HNO_2 + HNO_3$$

and the secondary decomposition reaction:

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$$

lead to the formation of solutions of nitric rather than nitrous acid, especially as the decomposition of nitrous acid is acid catalyzed. In one investigation[13] less than 1% of nitrous acid was found. These reactions, which are of considerable technical importance, are rate-dependent upon the dinitrogen tetroxide concentration in the gas phase, and their kinetics are controlled by the chemical reaction between the dinitrogen tetroxide and water in the gas or gas-film phase.[14] Dinitrogen trioxide (equimolar concentrations of nitric oxide and nitrogen dioxide) reacts with water to give nitrous acid in higher concentrations than the comparable reaction employing nitrogen dioxide alone. In the gas phase[15] this reaction may have a half-change time as short as 0·014 sec., and is reported to involve a termolecular collision mechanism:

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

The reaction between water in the liquid phase and nitrogen dioxide–nitric oxide mixture has been the subject of many investigations, mostly of a technological nature, and it has been observed[16] that the concentration of nitrous acid formed decreases when the volume of water used as absorbent is reduced, and that relatively more nitric acid is formed. Research into this reaction has been reviewed.[16] The formation of nitrous acid by the reduction of nitric acid with nitric oxide (Mellor, VIII, 456):

$$H_3O^+ + NO_3^- + 2NO \rightarrow 3HNO_2$$

can be seen to be related to the reverse of the decomposition reaction and to the action of dinitrogen trioxide on water. The rate of reaction of nitric oxide with nitric acid[17–21] is proportional to the hydrogen ion concentration, the nitrate ion concentration and the nitrous acid concentration and the reaction is therefore autocatalytic; it is independent of the nitric oxide partial pressure and is decreased slightly by increased ionic strength.[19] Nitrous acid formation is considered[19] to occur by a two-stage reaction:

$$\text{(i)} \qquad H_3O^+ + NO_3^- + HNO_2 \xrightarrow{k_1} N_2O_4 + 2H_2O$$

$$\text{(ii)} \qquad N_2O_4 + 2NO + 2H_2O \xrightarrow{k_2} 4HNO_2$$

k_1 being rate-determining for the overall reaction and having the value[21] 1·6 l.^{2} mole^{-2} min.$^{-1}$ at 25°C. The more empirical aspects of the efficiency of the absorption of mixtures of nitric oxide and oxygen in nitric acid as compared with alkali have been the subject of study,[22, 23] and it has been shown that alkaline absorption is industrially advantageous.

In the laboratory solutions of nitrous acid are best prepared by acidification of a nitrite with a mineral acid or other moderately strong acid. Solutions containing only nitrous acid have been prepared by this method by causing silver nitrite to react with hydrochloric acid or barium nitrite with sulphuric acid in equivalent proportions.

Physical Properties

All attempts to isolate 100% nitrous acid have been unsuccessful because of the extensive decomposition that results. Dilute solutions of the acid can be prepared but the decomposition reaction:

$$3HNO_2 \rightarrow H_3O^+ + NO_3^- + 2NO$$

limits the useful life of such solutions. The thermodynamic equilibrium defined as $[HNO_3]f_{HNO_3}p_{NO}^2/[HNO_2]^3f_{HNO_2}^3$ has been determined[21, 24–6]; the values (the nitrous acid activity function assumed as unity) being[26] 29·4 atm.^{2} l.^{2} mole^{-2} at 298° Abs., 50·8 atm.^{2} l.^{2} mole^{-2} at 308° Abs. and 80·1 atm.^{2} l.^{2} mole^{-2} at 318° Abs. The variation of equilibrium constant with temperature gives an estimated value of 10·2 kcal./mole for the enthalpy change. The rate of the decomposition of nitrous acid has been investigated[18–20, 27–28] and has been found to be proportional to the fourth power of the undissociated nitrous acid concentration and inversely proportional to the square of the nitric oxide concentration. The rate of variation of the nitrous acid concentration in the equilibrium system nitrous acid–nitric oxide–nitric acid is given by[21]:

$$\mp d[HNO_2]/dt = (\pm k_1 a^3_{HNO_2}/p^2_{NO} \mp k_2 a_{H^{\cdot}} a_{NO_3})[HNO_2]$$

where k_1 has the value 46 at 25°C. and k_2 the value 1·6, concentrations being in moles/l., pressures in atm., and time in min. The effects of temperature and concentration on k_1 have also been measured[29] and the abnormally high temperature coefficient has led to the suggestion of the following mechanism:

$$\text{(i)} \qquad 4HNO_2 \rightleftharpoons N_2O_4 + 2NO + 2H_2O$$

$$\text{(ii)} \qquad N_2O_4 + H_2O \rightleftharpoons HNO_2 + HNO_3 \text{ (equilibrium constant } k\text{)}$$

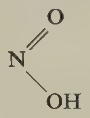
From the temperature dependence of *K*, the enthalpy change for reaction (ii) is estimated to be 21·2 kcal. The rate of decomposition of nitrous acid is increased by passing an inert gas through its solution[30, 31] and the reaction is also accelerated by hydrochloric acid,[32] probably through the formation of nitrosyl chloride. Air increases the rate of decomposition even more than an inert atmosphere.[31, 33, 34] Light accelerates the decomposition[35]; in the wave-length range 4725–8500 A., the velocity is proportional to the cube root of the light intensity. Nitrous acid solutions in hermetically sealed vessels[36, 37] decompose more slowly than in a gaseous atmosphere, presumably because the evolved nitric oxide inhibits further decomposition since it favours the reverse reaction. A similar effect is believed to operate in the stabilization of the acid by liquid petrolatum.[36, 38] Phthalic anhydride, potassium oxalate, molybdic acid,[38] sucrose, glucose, glycerol, ethanol, diethyl ether, hydroquinone, phenol and some alkaloids[39] are all reported to reduce the rate of decomposition of nitrous acid.

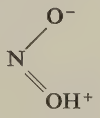
Nitrous acid is a weak monobasic acid; its acid dissociation constant has been determined conductimetrically[40, 41] and potentiometrically,[42] the values so found being shown in Table I.

Table I.—Dissociation Constant of Nitrous Acid

	Temperature °C.					Reference
	0	12·5	20·0	25·0	50·0	
Dissociation constant mole/l.$^{-1} \times 10^4$	3·2 (±0·3)	4·6 (±0·4)				40
	3·5			5·1	7·1	41
			7			42

That the hydrogen in nitrous acid is bonded to oxygen (rather than to nitrogen) has been shown by magnetic susceptibility measurements.[43] Structurally the acid exists both in the *cis* and *trans* form, the *trans* acid being more stable as shown by infra-red spectroscopic studies.[44–49] On this evidence the following resonance structures are considered to contribute to the structure of the acid;[45–46] the contribution of structure III explains why the *trans* form is the more stable:


I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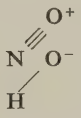

III

Analysis of the infra-red spectrum of nitrous acid, which shows absorption frequencies due to both *cis* and *trans* isomers, results in the following values for the interatomic bond dimensions: O–N bond length = 9·98 A., NO–N bond length = 1·46 A., N–O bond length = 1·20 A., N–O–N angle = 103° for *cis* and 105° for *trans*, O–N–O angle = 114° for *cis* and 118° for *trans*. The energy difference between the two forms has been estimated from pure spectroscopic[48] and matrix isolation data[49] to be of the order of 500 g.-cal. mole^{-1}. This value is,[49] however, difficult to rationalize with the value of 12 kcal. mole^{-1} reported for the energy barrier to rotation.[44, 45] From spectroscopic data the entropy and heat capacity for both isomers and for the mixture of these present in nitrous acid have been calculated at various temperatures, together with the ratio of concentrations of *trans* to *cis* isomer present[48]: these are reproduced in Table II.

The ultra-violet absorption spectrum of nitrous acid has been examined.[50] The heat of formation of nitrous acid has been reported[29] as −29·1 kcal. mole^{-1}.

Table II.—Entropy and Heat Capacity of Nitrous Acid

Temperature °K.	*trans* acid		*cis* acid		Equilibrium mixture		Composition ratio *trans*:*cis*
	C_p° kcal. mole^{-1}	S° e.u.	C_p° kcal. mole^{-1}	S° e.u.	C_p° kcal. mole^{-1}	S°* e.u.	
100	8·03	49·61	8·03	49·71	8·03	51·00	13
200	9·33	55·50	9·24	55·58	9·31	56·90	3·6
250	10·21	57·67	10·07	57·72	10·17	59·06	2·8
275	10·63	58·67	10·48	58·71	10·59	60·06	2·5
298·16	11·00	59·54	10·84	59·57	10·95	60·93	2·3
300	11·03	59·61	10·87	59·64	10·98	61·00	2·3
325	11·42	60·51	11·25	60·52	11·37	61·89	2·2
350	11·78	61·37	11·61	61·37	11·73	62·75	2·1
400	12·44	62·98	12·28	62·96	12·38	64·35	1·9
500	13·55	65·83	13·42	65·83	13·50	67·24	1·7
600	14·42	68·43	14·32	68·36	14·38	69·78	1·5
700	15·11	70·71	15·05	70·62	15·08	72·05	1·4
800	15·68	72·76	15·64	72·67	15·66	74·10	1·4
900	16·15	74·64	16·14	74·54	16·15	74·98	1·3
1000	16·56	76·36	16·56	76·27	16·55	77·70	1·3

* The entropy of mixing, ***R*** ln 2, has been added

Figure 1 shows the vapour pressure of nitrous acid as a function of its concentration in aqueous solution[51]; it is reported that the vapour is essentially nitrous acid and not dinitrogen trioxide. The activity function of aqueous nitrous acid has been determined[21] as a function of ionic strength.

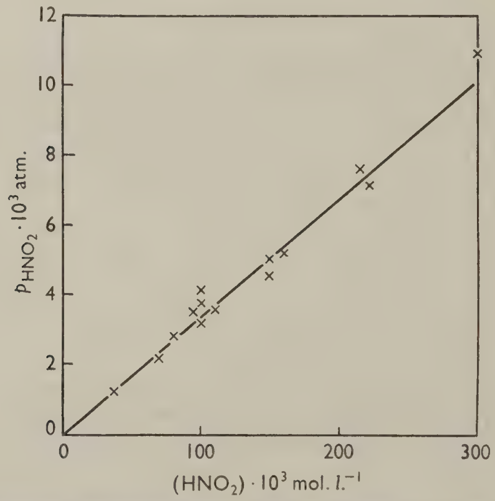


FIG. 1.—Vapour pressure of aqueous nitrous acid as a function of its activity at 25°C and ionic salt strength 1·4 molar

Chemical Properties and Reactions

OXYGEN-EXCHANGE WITH WATER

Nitrous acid exchanges its oxygen with water,[52–55] the reaction being a nucleophilic displacement:

$$H_2{}^{18}O + HO.NO \rightleftharpoons N^{18}O.NO + H_2O$$

This reaction, which catalyzes the oxygen exchange between water and nitric acid,[52–53] is considered to involve the nitrous acidium ion $H_2NO_2^+$ (which can be considered as a solvated nitrosonium ion NO^+) as follows[54–55]:

$$2HNO_2 \rightleftharpoons H_2NO_2^+ + NO_2^-$$

followed by the rate-determining reaction with nitrite ion:

$$H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O$$

Weak anions catalyze this exchange since the reactions:

$$H_2NO_2^+ + X^- \rightleftharpoons NO.X + H_2O$$

and

$$NO.X + NO_2^- \rightleftharpoons N_2O_3 + X^-$$

proceed in competition with the reaction between the nitrous acidium ion and nitrite ion. This reaction scheme is applicable to the majority of the reactions of nitrous acid, the substrate which reacts being either the nitrous acidium ion or the nitrosonium ion, and such mechanisms show hydrogen-ion catalysis (since the acidity favours the formation of the nitrous acidium ion) and catalysis (in many cases) by weak anions such as acetate and phosphate ions. The equilibrium between nitrous acid and the nitrosonium or nitrous acidium ion has been studied in perchloric acid[50, 56] and the free energy of formation of the nitrosonium ion estimated[56] as 5·7 kcal. mole^{-1} at 25°C. In concentrated sulphuric acid there is evidence[57] for the equilibrium:

$$HO.NO + 2H_2SO_4 \rightleftharpoons NO^+ + H_3O^+ + 2HSO_4^-$$

Such mixtures are of importance in the lead chamber process for the manufacture of sulphuric acid and have been investigated from this technical aspect.[58, 59]

REACTIONS WITH HYDRAZOIC ACID, HYDROXYLAMINE AND UREA

Hydrazoic acid reacts with nitrous acid to give nitrous oxide, nitrogen and water:

$$HNO_2 + HN_3 \rightarrow H_2O + N_2O + N_2$$

and this reaction has been recommended for use in the determination of nitrites in the presence of nitrates, since no nitric acid is formed from the nitrous acid under the conditions of the experiment.[60, 61] The rate of reaction is proportional to the nitrite ion activity and to the square of the hydrogen ion activity and is independent of the azide activity. This reaction is considered[62] to involve the formation of the nitrosonium ion as the rate-determining step, this ion then reacting with the azide ion as follows:

$$NO^+ + N_3^- \rightarrow N_2 + N_2O$$

The experimental rate of reaction is given by[62]

$$\boldsymbol{RT}/Nh \exp(12/\boldsymbol{R} - 12{,}800/\boldsymbol{RT}).\ a_{\mathrm{NO_2}} - a_H{}^{+2}/f_x,$$

where a are activities, and f_x is the activity function of the transition state. Confirmatory evidence that this reaction scheme involves the nitrosonium ion has come from investigations[63, 64] employing ^{15}N substituted sodium azide, $NaN^{15}NN$ and $NaNN^{15}N$. A study[63, 64] of the isotopic reaction, which can be written as

$$\mathrm{H\underset{\mathit{a}}{N}\underset{\mathit{b}}{N}\underset{\mathit{a}}{N} + H\underset{\mathit{c}}{N}O_2 \rightarrow \underset{1}{N}\underset{2}{N}O + \underset{3}{N}\underset{3}{N} + H_2O},$$

indicated that the c nitrogen was equivalent to the 2 nitrogen, the a nitrogen was equivalent to the 1 nitrogen and the a, b nitrogens were equivalent to the 3 nitrogens. This implied that the reactions occurring are:

$$\mathrm{\underset{\mathit{a}}{N}\underset{\mathit{b}}{N}\underset{\mathit{a}}{N}^- + \underset{\mathit{c}}{N}O^+ \rightleftharpoons \underset{\mathit{a}}{N}\underset{\mathit{b}}{N}\underset{\mathit{a}}{N}\underset{\mathit{c}}{N}O \rightarrow \underset{\mathit{a}}{N}\underset{\mathit{b}}{N} + \underset{\mathit{a}}{N}\underset{\mathit{c}}{N}O}$$

Refs. p. 363

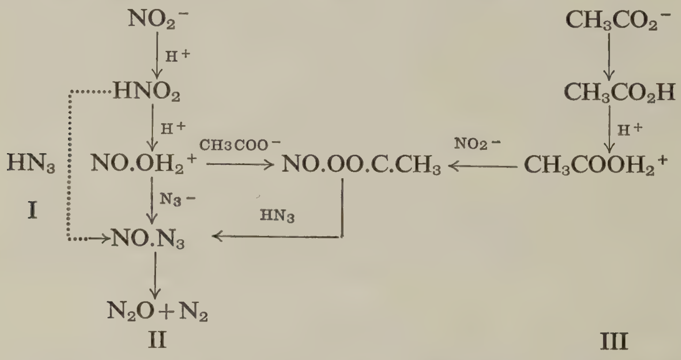
A recent extensive study of this reaction[65] has shown that other reaction paths may occur. In the absence of buffers and at high azide and low nitrite concentrations and in the presence of a series of anions (including nitrate, chloride, bromide and iodide) the reaction was found to follow the kinetics:

$$-\frac{d[NO_2^-]}{dt} = (k_1[N_3^-]+k_2[X^-])[NO_2^-][H^+]^2$$

where X^- stands for the generic anions, NO_3^-, Cl^-, Br^- or I^-. The dependence of the reaction on the azide concentration indicates that the formation of nitrosonium ion is a precursor to reaction and that the rate-determining step is its reaction with azide or X^-, in the latter case followed by:

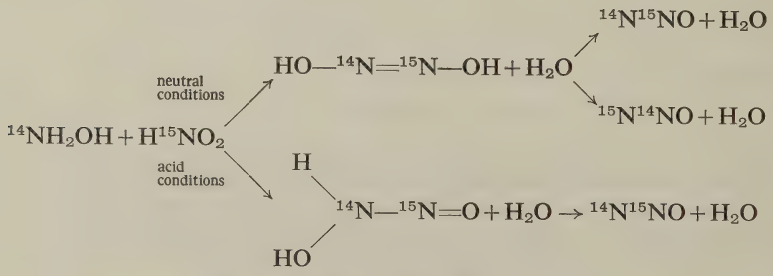
$$NO.X+N_3^- \rightarrow NO.N_3+X^- \text{ etc.}$$

In the presence of weak buffer anions such as acetate or phosphate the reaction is much faster[65] owing to a faster reaction path involving the intermediate acetyl nitrite (or phosphate); the overall scheme is envisaged as:



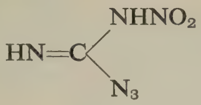
It is estimated that the reaction via route III proceeds 15 times as fast as that via route II, the side reaction I occurring to a minor extent.

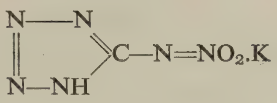
With hydroxylamine, nitrous acid gives[66] nitrous oxide and water and traces of hyponitrous acid ($H_2N_2O_2$); the last compound is an intermediate in the reaction. The reaction has been studied kinetically,[66–68] the most recent work employing both isotopic nitrogen and oxygen as tracers. The results indicated the following reaction paths; these paths are consistent with the isotopic trace studies employing nitrogen labelling:



The ratio in an acid medium $[^{14}N^{15}NO]/[^{15}N^{14}NO]$ was 2, and tended to unity in neutral solution so confirming the proposed mechanism. The oxygen exchange using ^{18}O-enriched water is acid-catalysed and occurs exclusively via the nitrous acid or unsymmetrical intermediate formed.[68]

Urea reacts with nitrous acid to form nitrogen, carbon dioxide and water. This reaction has been of use in removing nitrous acid from industrial sodium nitrate.[69] Substituted ureas, notably guanidine and nitroguanidine, react with nitrous acid, the former reacting only in acid solution giving cyanamide.[70–71] The latter is reported[72] to give nitroguanyl azide (I) in acid solution whilst the potassium salt of 5-nitroamino-1-H-tetrazole (II) is formed in neutral or weakly acid (acetic) potassium nitrite solution.


(I)


(II)

OXIDATION OF NITROUS ACID

The oxidation of nitrous acid by atmospheric oxygen, which does not occur with neutral or alkaline nitrite solutions, is known to proceed by oxidation of the nitric oxide formed by decomposition of the acid[73–75]; the resulting nitrogen dioxide reacting as the dimer with water to give equimolar amounts of nitric acid and nitrous acid. Both these steps have already been discussed.

Hydrogen peroxide oxidizes nitrous acid to nitric acid with the probable formation of pernitrous acid HNO_3, an isomer of nitric acid, as an intermediate. It has been shown[76] that on making a freshly acidified solution of alkali nitrite and hydrogen peroxide alkaline, 70% of the nitrite appears as the alkali pernitrite. This pernitrite is stable in alkaline solution but decomposes in acid conditions. The rate of hydrogen peroxide oxidation is[77–80] proportional to the concentrations of nitrous acid, hydrogen peroxide and hydrogen ion, although one investigator[77] reports that the rate is also dependent on a second additive term proportional to the hydrogen peroxide concentration and to the square of the nitrous acid concentration. Various mechanistic schemes have been invoked to explain the kinetic dependences found, but only those involving pernitrous acid as an intermediate will be considered further. Because the reaction mixture initiates the polymerization of methyl acrylate and the formation of phenol from benzene, it has been suggested[78] that free hydroxyl radicals are formed. A reaction scheme consistent with this contention has been proposed[78]:

(i) $HNO_2 + H_2O_2 \rightarrow HO_2.NO + H_2O$

(ii) $HO_2.NO \rightarrow HO^{\cdot} + NO_2^{\cdot}$

(iii) $HO^{\cdot} + NO_2^{\cdot} \rightarrow H^+ + NO_3^-$

with reaction (i) being rate-determining at low acidity. At high acidity (0·1–0·2 N. acid) it is suggested[78] that the pernitrous acid may be formed by the reactions:

(iv) $HNO_2 + H^+ \rightarrow NO.OH_2^+$ (or $NO^+ + H_2O$)

(v) $NO^+ + H_2O_2 \rightarrow HO_2NO + H^+$

Another suggested mechanism[79] is that the pernitrous acid formed by reaction similar to (i) and written as $HO_2^-.NO^+$ reacts slowly in the reverse manner to reaction (v) to regenerate hydrogen peroxide and the nitrosonium ion, the reaction then proceeding as follows:

(vi) $NO^+ + H_2O_2 \rightarrow NO^+.OH^{\cdot} + OH^{\cdot}$

(vii) $NO^+.OH^{\cdot} + OH^{\cdot} \rightarrow NO^+(OH)_2$

(viii) $NO^+(OH)_2 \rightarrow NO_2^+ + H_2O$

(ix) $NO_2^+ + OH^- \rightarrow HNO_3$

A recent study[80] of the ^{18}O exchange occurring during reaction has shown that the presence of hydrogen peroxide markedly inhibits the normal ^{18}O exchange between nitrite ion and water, and this can only be explained by competition between water and hydrogen peroxide with a common active intermediate, presumably the nitrous acidium ion or the nitrosonium ion. At nitrite concentrations that are low compared with that of hydrogen peroxide, two ^{18}O atoms were transferred from each molecule of hydrogen peroxide for each nitrate ion formed; high nitrite concentrations resulted in only one such ^{18}O atom being transferred. The following mechanism was therefore proposed:

$$HNO_2+H^+ \rightarrow NO.OH_2^+ \text{ (or } NO^+ +H_2O)$$
$$NO.OH_2^+ \text{ (or } NO^+)+H_2{}^{18}O_2 \rightarrow ON.{}^{18}O.{}^{18}OH+H_3O^+$$

at high nitrite concentration:

$$ON.{}^{18}O.{}^{18}OH+NO_2^- \rightarrow ON{}^{18}O^- + {}^{18}ONO_2^- +H^+$$

at low nitrite concentration:

$$ON.{}^{18}O.{}^{18}OH \rightarrow {}^{18}O_2NO^- +H^+$$

The action of nitric acid on nitrous acid with the formation of oxides of nitrogen, in particular dinitrogen tetroxide, has been discussed.[81–82]

REDUCTION OF NITROUS ACID

Nitrous acid is reduced by hydrogen sulphide to give nitric oxide and some nitrous oxide[83] when the acid is in excess. An excess of hydrogen sulphide leads to the formation of ammonia and hydroxylamine, the former being the major product under acid conditions.[83] Nearly all the hydrogen sulphide is oxidized to elemental sulphur although in concentrated nitrous acid traces of sulphur trioxide are formed.[83] It has been suggested[84] that hydrogen sulphide be used to remove nitric and nitrous acid from sulphuric acid.

It has been reported[85] that sulphur monoxide obtained by the burning of sulphur at reduced oxygen pressures reacts with nitrous acid in concentrated sulphuric acid.

Sulphur dioxide (or sulphurous acid) reduces nitrites and nitrous acid in weakly acid buffered solutions to give a salt of hydroxylaminesulphuric acid, which after isolation gives a hydroxylamine salt on acid hydrolysis.[86] The temperature for the reaction should be below 0°C. The kinetics and mechanism of the reaction have been investigated[87–88] (see also p. 116). In dilute acid solutions at normal temperatures sulphur dioxide reduces nitrous acid to a mixture of nitric and nitrous oxides,[89–92] the yield of nitrous oxide being increased by increased sulphur dioxide concentration as compared with nitrous acid concentration.[89–90] The overall reaction can be written as:

$$SO_2+2HNO_2 \rightarrow 2NO+H_2SO_4$$

and

$$H_2O+2SO_2+2HNO_2 \rightarrow 2H_2SO_4+N_2O$$

with a reaction scheme involving either the HNO radical[89–90] or the nitrosonium ion,[91] thus:

(i) $$SO_2+HNO_2 \rightarrow SO_3+HNO$$

followed by:

$$2HNO \rightarrow N_2O+H_2O$$

or at high $[HNO_2]$:

$$HNO+HNO_2 \rightarrow 2NO+H_2O$$

or

(ii)
$$\begin{aligned}&2(HNO_2 \rightleftharpoons OH^- +NO^+)\\&NO^+ +SO_2 \rightarrow NO+SO_2^+\\&NO^+ +SO_2^+ \rightarrow NO+SO_2^{2+}\\&SO_2^{2+} +2O^{2-} \rightarrow SO_4^{2-}\\&2(OH^- \rightleftharpoons O^{2-} +H^+)\end{aligned}$$

With thiosulphate ion, nitrous acid reacts in acid solution to give nitric oxide and the tetrathionate ion, and the kinetics of this reaction have been studied.[92] Nitrous acid reacts with the nitrosyldisulphonate ion[93–94] to give nitrous oxide and sulphate ion, and kinetic studies indicate the following mechanism, the first step being rate-determining[93–94]:

(i) $2HNO_2 \rightarrow N_2O_3 + H_2O$

(ii) $(SO_3)_2NO^{2-} + N_2O_3 + 2H_2O \rightarrow 2SO_4^{2-} + NO^+ + NO + NOH + H_3O^+$ fast

(iii) $(SO_3)_2NO^{2-} + NO + H_3O^+ \rightarrow (SO_3)_2NOH^{2-} + NO^+ + H_2O$ fast

(iv) $2NOH + NO^+ \rightarrow HNO_2 + N_2O$

The reaction of nitrous acid, or of a nitrite in acid solution, with aminosulphonic acid is of importance as an analytical technique in the determination of nitrites[95–99] especially in the presence of large quantities of nitrate. The reaction is:

$$MNO_2 + H_2NSO_3H \rightarrow MHSO_4 + N_2 + H_2O$$

and the sulphate is usually determined,[95–96] as determination of the evolved nitrogen is reported[97] to be in error owing to slight nitrogen oxide formation, although this can be allowed for.[97] The reaction has been studied kinetically.[99]

Nitrous acid oxidizes arsenious acid and if present as an impurity in nitric acid accelerates the oxidation of arsenious acid by nitric acid.[100] The overall reaction, which is catalysed by chloride ion,[100, 101] can be represented by:

$$H_3AsO_3 + 2HNO_2 \rightarrow H_3AsO_4 + 2NO + H_2O$$

The oxidation of ferrous ion by nitrous acid in acid solution is known[102–3] to be due to the simultaneous oxidation by nitrogen dioxide (from the decomposition of the nitrous acid) and by the nitrosonium (or nitrous acidium) ion. The overall reaction which has the stoicheiometry:

$$Fe^{2+} + HNO_2 + H^+ \rightleftharpoons Fe^{3+} + NO + H_2O$$

is governed by an equilibrium whose equilibrium constant,

$$[Fe^{3+}]p_{NO}/[Fe^{2+}][HNO_2][H^+]$$

has the value[103] $9{\cdot}2 \times 10^3$ atm. mole^{-2} l.^{2} at 25°C. The kinetics are represented by the expression[103]:

$$\frac{d[Fe^{3+}]}{dt} = (k_1 + k_2[H^+] + k_3[HNO_2]/p_{NO})[Fe^{2+}][HNO_2]$$

where the values of k_1, k_2 and k_3 at 25°C. are 0·47, 13·6 and 240 (in mole l.$^{-1}$, atm. and min. as basic units) respectively. These findings are consistent with the reaction paths[102–103]:

(i) $2HNO_2 \rightleftharpoons NO_2 + NO + H_2O$

(ii) $Fe^{2+} + NO_2 \xrightarrow{k_4} Fe^{3+} + NO_2^-$

(iii) $HNO_2 + H^+ \rightarrow H_2O + NO^+$

(iv) $Fe^{2+} + NO^+ \rightarrow Fe^{3+} + NO$,

the nitric oxide formed acting as a negative autocatalyst. The value of k_4 has been estimated[103] to be $1{\cdot}3 \times 10^4$ atm.$^{-1}$ min.$^{-1}$ at 25°C.

MISCELLANEOUS OXIDATIONS AND REDUCTIONS

Nitrous acid is oxidized by dichromate ions in acid solution to nitric acid; this reaction is stated[104] to be catalysed by foreign undissociated acid molecules and a study of its kinetics indicates that the nitrous acid molecule rather than the nitrite ion is oxidized. Oxidation by dichromate[105] has been studied as an analytical method for nitrite determination as have the oxidants manganic sulphate[105] and ceric salts.[106] Potassium ferrocyanide reduces nitrites to nitric oxide quantitatively.[107] In many cases concurrent potentiometric studies have been carried out.[106–107]

Hypochlorites oxidize nitrites in acid solution,[108] the reaction ceasing at pH values above 10. Chlorates, bromates and iodates oxidize nitrites[104, 109, 110]: the reactions are of the second order, the substrate being the nitrous acid molecule, are acid catalysed and do not occur in neutral solutions. Chloride and bromide ions are reported[110] to have no effect on the reactions of the corresponding chlorates and bromates with nitrous acid.

Nitrous acid reacts with iodides to give iodine and nitric oxide; the reaction is slow[111] and is catalysed by oxygen[112–113] (owing to the formation of more nitrous acid from the nitric oxide). The major reaction is:

$$2HNO_2 + 2HI \rightarrow 2NO + I_2 + 2H_2O$$

although it is reported[42] that this is not always the only reaction operative. In 2 to 7·5 N. sulphuric acid nitrous oxide as well as nitric oxide is formed by the competing reaction:

$$2HNO_2 + 4HI \rightarrow 2I_2 + N_2O + 3H_2O$$

which makes no measurable contribution in 10–15 N.-sulphuric acid.[42] In hydrochloric acid of concentration less than 5 N. reactions leading to both nitric and nitrous oxide occur, whilst above 5 N. acid concentrations the major reactions are[42]:

$$HI + 2HNO_2 + HCl \rightarrow ICl + 2H_2O + 2NO$$
$$HI + ICl \rightarrow HCl + I_2$$

The reaction is said to be unimolecular with respect to the iodide and nitrite concentrations and the velocity is proportional to the hydrogen ion concentration.[114] The effects of neutral salts and other unreactive substances on the reaction have been studied.[114, 115] It is reported that this reaction can be used for the determination of nitrites.[116]

Iodine reacts with nitrous acid:

$$HNO_2 + H_2O + I_2 \rightarrow 2HI + HNO_3$$

This reaction is considered[117] to proceed by two possible reaction paths:

(i)	(ii)
$NO_2^- + H^+ \rightarrow HNO_2$	$HNO_2 \rightarrow H^+ + NO_2^-$
$2(2HNO_2 \rightarrow NO_2 + NO + H_2O)$	$NO_2^- + I^+ \rightarrow NO_2 + I$ (rate determining)
$NO + I^+ \rightarrow NO^+ + I$ (rate determining)	$NO_2^- + I \rightarrow NO_2 + I^-$
$NO + I \rightarrow NO^+ + I^-$	$2NO_2 \rightarrow N_2O_4$
$2(NO^+ + OH^- \rightarrow HNO_2)$	$N_2O_4 + H_2O \rightarrow HNO_2 + H^+ + NO_3^-$
$2NO_2 \rightarrow N_2O_4$	
$N_2O_4 + H_2O \rightarrow HNO_2 + H^+ + NO_3^-$	

Nitrous acid attacks copper, a possible mechanism being[118]

$$HNO_2 + H^+ \rightleftharpoons H_2O.NO^+$$
$$Cu + H_2O.ON^+ \rightarrow CuNO^+ + H_2O$$
$$CuNO^+ + H^+ \rightarrow Cu^{++} + H\cdot + NO$$
$$H\cdot + HNO_2 \rightarrow H_2O + NO$$

It is well known that nitrous acid must be present in nitric acid before the latter will dissolve such metals as copper, silver or mercury. For copper a mechanism similar to that written above for the reaction with nitrous acid has been proposed,[119–120] as have mechanisms involving the formation of nitrogen dioxide which then attacks the metal.[120–122] It has also been suggested that the effect of nitrous acid is due to its action as a depolarizer[123–126] by the reaction[125–126]

$$NO_2 + e \rightarrow NO_2^-$$

This is consistent with the fact that the reduction of nitric acid occurs at a platinum cathode with the evolution of hydrogen, the reduction being autocatalytic (catalysed by nitrous acid).[123] The reduction of nitrous acid has been studied polarographically[127–130] and it is reported[128] that two half-wave potentials of $-0{\cdot}5$ v. and -1 v. are observed in acid solution, the former being due to the reduction of nitric oxide and the latter to the reduction of nitrous acid. It has been found that the nitrous acid reduction potential is very buffer-sensitive[130] and that in unbuffered acid solution the electrode processes are[129]:

$$HNO_2 + 4e + 5H^+ \rightarrow NH_2OH.H^+ + H_2O$$

and

$$NO_2^- + 4e + 6H^+ \rightarrow NH_2OH.H^+ + H_2O$$

It has been reported[131] that agitation of nitrous acid with mercury for 5 hours results in the partial reduction of the nitrous acid to form a little ammonia, a corresponding quantity of mercury being oxidized to mercurous oxide. The anodic oxidation of nitrous acid has been studied[132–134] and it is reported that oxidation occurs at a voltage of the order of 1 v.

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NITRITES

Preparation

Nitrites together with hyponitrites are said[1] to be found as intermediates in the bacteriological reduction of nitrates. Bacteriological oxidation of ammonia to nitrites by the action of methane-oxidizing bacteria is also known,[2] but the oxidation does not proceed further to nitrate. It has been suggested[3] that the photochemical oxidation of ammonia to nitrites and nitrates occurs in the atmosphere. The reduction of nitrates to nitrites can be effected by heat, light or ionizing radiations. The first method is used in the preparation both of nitrites of the alkali metals and to a lesser extent of the alkaline earth metals. The thermal decomposition of nitrates to nitrites can be carried out at a lower temperature and with a better yield by the addition of a reducing agent such as lead[4–6] or barium sulphide,[7] or by the use of a catalyst. The catalyst is usually an oxide of a metal having two valency states or of one having a higher oxide or peroxide,[8] barium oxide and manganese dioxide being particularly effective. This thermal decomposition is reversible but the reverse reaction is very slow[9–11] and so does not affect the industrial efficiency of the forward reaction. This, however, is disadvantageous with regard to the industrially important possibility of the oxidation of nitrite by gaseous oxygen which only occurs slowly at high oxygen pressures and is therefore commercially unprofitable[9–11] at the present time, since no catalyst is known for this reaction. The equilibria for these reactions are very dependent on the conditions since the reactions are heterogeneous.

Aqueous solutions of nitrates are reduced by the action of ultra-violet light[12] and this reaction is reversible. The reaction is faster in alkaline solution.[13] Sunlight is reported[13] to be ineffective in the atmospheric oxidation of nitrites unless a suspension of ferric oxide is present as catalyst. Irradiation of nitrates induces the reduction to nitrites,[14–18] the reverse reaction also occurring in aqueous solution; for example, in millimolar solution at pH 6 both reactions occur simultaneously, *X*-rays being the more efficient reducer and α particles the better oxidizer.[15] In solution the rate of nitrate reduction by γ rays has been found[16] to be independent of the cation, dependent on the nitrate concentration and dependent on the total energy absorbed by the solution. Studies have also been made in a heavy-water pile and with low energy *X*-rays[17] and it has been concluded that electron ionization rather than collision excitation by the particles causes the decomposition. An extensive investigation[18] of the reduction of the solid nitrates of the alkali metals, strontium, barium and silver by *X*-rays has been carried out: yields are reported together, in some cases, with their variation with temperature, changes in infra-red spectra, and in the case of potassium nitrate the kinetics of the decomposition.

The alkali and alkaline earth nitrites are usually prepared industrially by the absorption of oxides of nitrogen (mixtures of nitric oxide and nitrogen dioxide) in solutions of the hydroxide, carbonate or sulphide. There is an extensive technological literature in this field[19–41] and some studies of the optimum conditions for these reactions have been reported.[42–46] The rate of absorption of oxides of nitrogen is not decreased but rather slightly increased as the reaction proceeds,[46] and initial high alkali strength led to lower initial rates of absorption.[46] With sodium hydroxide in the range 17–65°C. temperature effects have been shown[46] to be negligible. The more technical aspects of this reaction have been reviewed in two papers: the first[47] covering the period 1933–1939 and the second[48] the period 1939–1941. The absorption of oxides of nitrogen has been used on the laboratory scale to prepare nitrites as described under the individual nitrites.

The possibility of the oxidation of ammonia followed by immediate absorption on an alkaline surface to form a nitrite or nitrate has been investigated using both thermal[49] and electrochemical[50] oxidation. The former method is effective at temperatures of 400°C. and even lower, especially in the presence of catalysts such as copper, nickel, cobalt or silver. Electrochemical oxidation in conjunction with absorption has been found[50] in the cell:

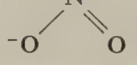
$$\mathrm{O_2(Pt)}\left|\begin{matrix}\mathrm{KOH+NaOH}\\ \text{fused}\end{matrix}\right|\mathrm{(Pt)NH_3}$$

On short circuiting the cell for several hours nitrate was found at 250°C. and nitrite between 250 and 350°C. This reaction was catalysed by the platinum cathode and by such trace substances as nickel oxide, copper oxide, alkali nitrate and water. The oxidation of nitrogen to its oxides has been carried out[51] in a gas battery, and by using an alkaline electrolyte nitrites are formed.

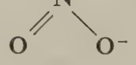
In the laboratory nitrites can be prepared by modifications of the industrial methods. Reduction of the nitrate is usually carried out by employing spongy lead (obtained by the action of lead acetate on magnesium) and the lead is finally removed as the carbonate by passing carbon dioxide through the solution. Double decomposition reactions between silver nitrite (obtained from sodium nitrite and silver nitrate) and metal halide or between barium nitrite and metal sulphate are efficacious in the laboratory preparation of some nitrites as the insoluble silver chloride or barium sulphate may be filtered off, leaving the nitrite in solution.

General Properties of the Nitrite Ion

Structurally the nitrite ion belongs to the space group C_{2v} as it is not linear but bent. Two resonance structures:



and



are postulated[52] and a calculation on this ion by the method of linear combination of atomic orbitals (L.C.A.O.) which was attempted[52] predicted a N–O bond length of 1·257 A. The individual bond lengths and angles for various nitrites are reported under the nitrites concerned. In aqueous solution the ion is believed to exist with one molecule of water of solvation as estimated from vapour pressure data.[53] The ionic conductance of the nitrite ion has been determined[54] as 55·0 mhos cm.^{2} in methanol at 25°C. and as 25·9 mhos cm.^{2} in ethanol at 25°C. A value of 9·28 c.c.$^{-1}$ for the molar refractivity of the nitrite ion is quoted in the literature.[55] This ion is diamagnetic and its susceptibility has been determined[56–57] by measurements of the susceptibility of sodium, potassium and barium nitrites as $8{\cdot}0 \times 10^{-6}$ c.g.s. units for the solid and $11{\cdot}4 \times 10^{-6}$ c.g.s. units for the aqueous solution.

The polarographic reduction of the nitrite ion at the dropping mercury cathode proceeds only in the presence of highly charged ions[58–60] such as lanthanum, cerous and uranyl cations, and molybdates. The principal products of this reduction are ammonium ion and hydroxylamine, the latter being the major product in one investigation[59] of the reduction of the nitrate ion (which proceeds via the nitrite ion) in the presence of uranyl salts. Neutral or alkaline solutions of nitrites are not reduced at the mercury cathode in the absence of highly charged ions. A recent investigation[61] reports discontinuities when the nitrite is reduced; this is taken as evidence of a 'slowed-down' reaction between the electrode and the reducible anion. Furthermore, evidence of a hysteresis effect[61] was said to indicate that the reaction products could be transferred from one mercury drop to another and so influence the concentration-dependence of the electrode process. Such effects complicate any study of these reduction phenomena. In comparing the potentials of silver, copper and platinum cathodes in contact with buffered sodium nitrite solutions[62] it was found that the potential of the platinum electrode is considerably the highest. Nitrites depolarize anodes exhibiting oxygen overpotential[63]: the addition of 0·01 M. sodium nitrite to a phosphate buffer of pH 6·8 raised the oxygen overpotential of a platinum wire anode by 0·17 v. at 20°C. when a current of current density 0·15 amp. cm.$^{-2}$ had previously been passed for 2 mins. This effect is specific to platinum and does not occur with gold, palladium, graphite or nickel anodes.[63]

The presence of nitrites inhibits the corrosion of ferrous and non-ferrous metals such as aluminium,[64] tin[65] and tin plate,[66] and chromium.[67] The use of nitrites as corrosion inhibitors is of great industrial importance as can be seen by the numerous papers and patents dealing with technological and practical applications of nitrites in this field,[68–112] as well as with the optimum conditions for corrosion inhibition and the underlying mechanisms.[113–128] The nitrite ion passivates the metal by the formation of a uniform layer of oxide[125–128] (Fe_2O_3 in the case of iron) the nitrite ion taking a part in the formation and repair of such films, though these are believed to be formed by the oxygen dissolved in the aqueous solution rather than by that combined chemically in the nitrite.[126]

Nitrites do not undergo oxidation by gaseous oxygen unless a catalyst or carbon dioxide is present. In the presence of the latter the oxidation is exclusively due to the oxidation of the nitrous acid set free.[129] Ferrous hydroxide[130–132] and other insoluble iron-containing materials[133] induce the oxidation of nitrite solutions by oxygen to give nitrate. Photo-oxidation of nitrites also occurs in the presence of catalysts such as ferric oxide, zinc oxide and even soil.[134–135] It has been said[136] that the oxidation of nitrites to nitrates in the soil is a purely physicochemical process, microbiological reaction playing no significant part; on the other hand, photochemical oxidation is said[136] to contribute only to an insignificant extent to this oxidation in soil. Nitrites are oxidized by nitric acid or by oxides of nitrogen and oxygen to nitrates and as this reaction is of industrial importance, particularly for the conversion of sodium nitrite to nitrate, the technological details and the most favourable conditions for conversion have been studied.[137–143]

It has been reported[144] that nitrites may be quantitatively reduced in neutral or alkaline solution by boiling with ferrous hydroxide; boiling alkali is said to give ammonia quantitatively whilst with boiling alkali carbonate some nitrous oxide is formed.

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DECOMPOSITION OF SOLID NITRITES

Nitrites in the solid state can be thermally decomposed to give a variety of products which may include the oxide, the nitrate, nitric oxide, nitrogen dioxide, nitrogen and oxygen as well as other products in specific cases (e.g., silver nitrite). For the alkali,[145–150] alkaline earth[151–153] and cadmium nitrites[154] the reactions occurring can be written in general as follows:

(i) $4NO_2^- \rightleftharpoons 2O^{2-} + 2NO + 2NO_2$

(ii) $O^{2-} + 2NO_2 \rightarrow NO_2^- + NO_3^-$

(iii) $NO_2^- + NO_2 \rightarrow NO_3^- + NO$

(iv) $2NO_2^- + 2NO \rightarrow 2NO_3^- + N_2$

(v) $2NO_3^- \rightarrow 2NO_2^- + O_2$

The major gaseous product is nitric oxide with increases in the nitrogen dioxide concentrations when the decomposition is excessively rapid.[150] Nitrogen is found only in small quantities[150–153] but its concentration increases if the nitric oxide produced in the reaction is allowed to remain at the reaction site.[150, 151] The temperature at which this decomposition begins, as indicated by the evolution of oxides of nitrogen, differs markedly for different nitrites, as shown in Table III.

Table III.—Estimated Decomposition Temperatures for the Nitrites

Nitrite	Decomposition temperature °C.	Reference
$LiNO_2$	200	155
$NaNO_2$	370	155
KNO_2	460	155
NH_4NO_2*	80	155
$AgNO_2$*	105	155
	101·6	156
$Ca(NO_2)_2$	316	151
	250	155
$Sr(NO_2)_2$	389	151
	350	155
$Ba(NO_2)_2$	362	151
	270	155

* Further mention of these nitrites is made under the appropriate sections. In the case of reference 155 the oxides of nitrogen were shown to be present by their action on starch-iodide solution.

Tracer studies[157] employing ^{13}N have shown that the exchange between nitrogen and aqueous nitrite is rapid but not immeasurably fast.

OXIDATION BY HALOGENS

The halogens oxidize nitrites to nitrates. The reaction most fully investigated is that of iodine[158–170] where the overall reaction is:

$$H_2O + NO_2^- + I_2 \rightarrow 2HI + NO_3^-$$

This reaction is photocatalysed: in the dark it is bimolecular,[158] and under ultraviolet radiation the Einstein law of photochemical equivalence does not hold.[159] Most of the earlier[160–165] reaction schemes involve the participation of the iodine cation and/or the hypoiodite ion as the oxidizing agent, the latter being formed from iodine atoms formed in turn from the iodine molecule. The reaction is now believed[166] to involve direct attack by iodine molecules to give iodine atoms and nitrogen dioxide as the primary step:

$$NO_2^- + I_2 \rightleftharpoons NO_2 + I^- + I\cdot \text{ (or } I_2^{-}\cdot)$$

followed by $$NO_2^- + I\cdot \rightleftharpoons NO_2 + I^-$$

and then $$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

This scheme is in agreement with the kinetic data[166] and with the rate of decomposition of nitrous acid. The photocatalysis can be explained by the same reaction scheme,[167] except that in this case the nitrogen dioxide results from the reaction of a nitrite ion with an iodine atom produced either by photodecomposition of an iodine molecule or by the reaction of a radiation-activated iodine molecule. The known effects that the quantum yield increases with increasing nitrite concentration and increases even more markedly with increasing iodine concentration can be explained[167] by this mechanism, as can the dependence of the reaction on temperature, ionic strength and wave-length of the exciting radiation. It has also been suggested[168] that this oxidation is induced by the addition of thiosulphate ions. More recently[169] it has been shown that nitrite is not consumed by the reaction with iodine in the presence of buffered (pH 6) thiosulphate but that the reaction between iodine and thiosulphate is induced by the nitrite. The reaction with thiosulphate involving nitrite as catalyst is believed to proceed by the following mechanism[169]:

$$I_2 + S_2O_3^{2-} \rightarrow S_2O_3I^- + I^-$$

or $$I_3^- + S_2O_3^{2-} \rightarrow S_2O_3I^- + 2I^-$$

followed by $$S_2O_3I^- + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + I^-$$

the normal iodine action on thiosulphate;
or in the presence of nitrite:

$$S_2O_3I^- + NO_2^- \rightleftharpoons S_2O_3NO_2^- + I^-$$

$$S_2O_3NO_2^- + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + NO_2^-$$

and $$S_2O_3NO_2^- + I_2 + 3H_2O \rightarrow 2SO_3^{2-} + 6H^+ + 2I^- + NO_2^-$$

the last step accounting for the formation of sulphate which is found after reaction,[169] since:

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2I^-$$

However, in the absence of a buffer or when nitrous acid is formed loss of nitrite will occur not only through decomposition but even more rapidly through reaction with thiosulphate.[170] This reaction is believed[170] to involve the nitrosonium (or nitrous acidium) ion as follows:

$$NO^+ + S_2O_3^{2-} \rightarrow S_2O_3^- + NO$$

$$S_2O_3^- + 7NO^+ + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 7NO$$

$$NO + I^+ \text{ (from } I_2) \rightarrow NO^+ + I$$

$$2I \rightleftharpoons I_2$$

Bromine also oxidizes nitrites to nitrates, the reaction being[171] unimolecular with respect to the bromine concentration and showing rate terms depending upon both the nitrite concentration and its square at constant bromine-bromide strengths. The last observation indicates that the reaction follows two independent paths, the experimental rate equation[171] being consistent with the scheme:

(i) $Br_2 + NO_2^- \rightleftharpoons Br_2NO_2^-$

(ii) $Br_2NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2Br^-$

or (iii) $Br_2NO_2^- + NO_2^- \rightleftharpoons Br(NO_2)_2^- + Br^-$

followed by (iv) $Br(NO_2)_2^- + H_2O \rightarrow HNO_2 + H^+ + Br^- + NO_3^-$

Steps (ii) and (iv) are rate-determining. This reaction is photocatalysed and has been investigated[172] under radiation of wave-length 436–365 mμ. The reaction mechanism proposed is very similar to that operative in the case of the iodine–nitrite reaction, except that the quantum yield found does not require secondary sources of activated bromine intermediates (molecules or atoms) after primary excitation.[172] The reaction can be explained[172] entirely by the primary photochemical formation of bromine atoms (probably from Br_3^-) followed by electron transfer from these to the nitrite ion to give nitrogen dioxide, which reacts further with water to give nitrous and nitric acids.

In the oxidation of nitrites by chlorine[173] the rate of reaction is found to be strongly dependent on pH, being practically instantaneous at and below pH 6. At higher pH values the velocity decreases with decreasing acidity and the reaction does not appear to go to completion, some of the chlorine and nitrite remaining unchanged. The position of equilibrium depends[173] upon the pH and initial concentrations of chlorine and nitrite and upon other factors such as temperature and the composition of the medium.

Nitrites may be oxidized by other oxidizing agents notably permanganates,[174] manganic salts[175] and ceric salts,[176] all of which react quantitatively under appropriate conditions and find application in the quantitative determination of nitrites. In this connection it has been recommended[175] that manganic sulphate rather than permanganate be used for this determination, since the former reacts very much faster and gives a sharper end-point.

The reduction of nitrites to ammonia by means of sodium polysulphide has been studied[177] and the individual reaction steps have been reported; these are complex in nature and many products containing sulphur are formed.[177]

Chemistry of the Individual Nitrites

Lithium nitrite has been prepared in the laboratory[155] by the action of a mixture of nitric oxide and nitrogen dioxide on a suspension of the oxide or carbonate. A purer product is obtained by using lithium oxide and a gas mixture in which the concentration of nitrogen dioxide is less than that of nitric oxide. The oxides of nitrogen are conveniently prepared by the gaseous oxidation of ammonia using a platinum catalyst. The reaction is stopped when all the oxide has gone into solution, thus avoiding the formation of the undesired nitrate which is only formed in acid solution. Excess of hydroxide remaining after the reaction is removed by concentrating the solution and then passing carbon dioxide through it to convert the hydroxide to the insoluble carbonate. Further concentration yields $LiNO_2,H_2O$ of 99·7% purity. The preparation from the carbonate[155] yields only a 90% pure product, the major impurity being bicarbonate which is difficult to remove.

Lithium nitrite exists with $\frac{1}{2}$, 1 or $1\frac{1}{2}$ molecules of water of crystallization[155, 178]; the hydrate $2LiNO_2,3H_2O$ is stable below −7·95°C. and at this temperature it loses water to give $LiNO_2,H_2O$ which in turn loses water to give $2LiNO_2,H_2O$ at 50·9°C. Dehydration to the anhydrous salt occurs[178] at 94°C. without melting. The anhydrous salt may be conveniently prepared[155] by exposing a hydrated form over phosphorus pentoxide in a desiccator. The phase diagram for the system lithium nitrite–water[178] is shown in Figure 2. The heats of solution and formation of anhydrous lithium nitrite are 2·38 kcal. mole^{-1} and 94·16 kcal. mole^{-1} respectively. Lithium nitrite monohydrate has[179] a monoclinic unit cell containing 4 molecular units and having sides a 3·31 Å., b 14·10 Å., c 6·36 Å., β 105°.

Sodium nitrite is reported[180] to be formed together with sodium amide, sodium hyponitrite and Na_2NO_2, when metallic sodium is added to ammonium nitrate in liquid ammonia. It is also found,[181] together with nitrogen dioxide, sodium hydroxide, ammonia and ammonium salts, when sodium nitrate is reduced by hydrogen gas under the influence of a 15 kv. discharge. Sodium nitrite has been prepared in the laboratory[155] by passing mixtures of nitric oxide and nitrogen dioxide through sodium hydroxide solution or through an aqueous solution of sodium carbonate; the former method gives a purer product, because when sodium carbonate is used sodium bicarbonate is formed as an impurity and is difficult to remove. The conditions for reaction are: that the nitrogen dioxide concentration in the oxides of nitrogen used (obtained by the catalytic oxidation of ammonia[155]) is less than the nitric oxide concentration, that the sodium hydroxide is free from carbonate and that the reaction is discontinued while the solution is still faintly alkaline to phenolphthalein. A 99·6% pure product is obtained[155] which is practically free from nitrate. This method of preparation has been used for the formation of sodium nitrite containing isotopic ^{15}N; in one case[182] the sequence of reactions was (i)

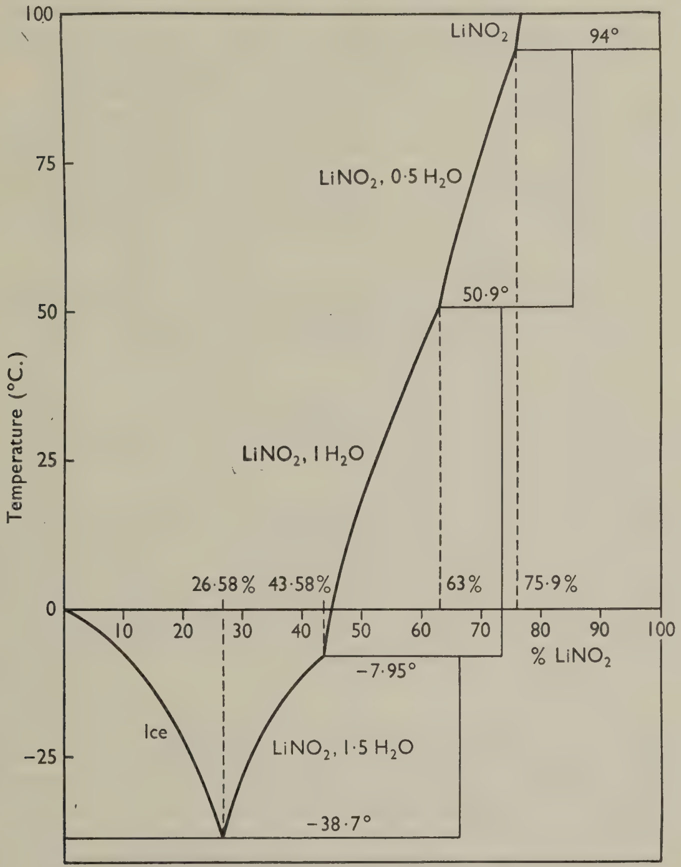

FIG. 2.—The system lithium nitrite–water

$^{15}N_2O$ was obtained by hypobromite oxidation of ammonium chloride rich in ^{15}N, (ii) oxidation of the nitrous oxide to nitrogen dioxide by means of a discharge, (iii) absorption of the ^{15}N rich nitrogen dioxide in water to give nitric acid, (iv) reaction with KOH to give the nitrate, (v) reaction of this nitrate with concentrated sulphuric acid and mercury to give ^{15}N rich nitric oxide, and (vi) absorption of this oxide in the presence of a calculated quantity of oxygen by sodium hydroxide to give sodium nitrite rich in ^{15}N. Another method described[183] was to convert ^{15}N rich-nitrogen into nitrogen dioxide by means of a high voltage arc, reduce the product with concentrated sulphuric and mercury to nitric oxide, which was then partially oxidized and adsorbed as described above. The reduction of fused sodium nitrate to the nitrite by the addition of metallic lead at 400–500°C. has been described,[184] but it is still necessary to neutralize the solution of the melt in water with oxides of nitrogen to obtain an alkali-free pure nitrite. This alkalinity is due to the formation of sodium oxide by thermal decomposition of the nitrite. A recent preparative method[185] yielding sodium nitrite of 99·95% purity is the reduction of the nitrate in the presence of sodium ferrate and nitric oxide at 400 ± 10°C. by the reaction:

$$NaNO_3 + Na_2Fe_2O_4 + 2NO \rightarrow 3NaNO_2 + Fe_2O_3$$

The reaction is carried out in vacuo, the heating being continued at 400°C. for 48 hours and for a further 72 hours at 360°C. if it is desired that the conversion be quantitative.[185] The industrial manufacture of sodium nitrite, which has already been discussed, leads to products which may contain considerable amounts of nitrate, carbonate and bicarbonate as impurities, and the action of atmospheric carbon dioxide on moist sodium nitrite causes further decomposition which may produce sodium nitrite containing a high percentage of these impurities; in one case,[155] as much as 40% was found. However, the purification of sodium nitrite presents no great difficulties[155, 186]; four recrystallizations of the 60% sample mentioned above gave a 99·37% pure product. The remaining impurity of sodium carbonate could be removed by recrystallization from 50% alcohol to give a 99·45% pure product; alternatively for a product of 99·7% purity in rather low yield a further recrystallization from 80% alcohol suffices.

Because inadequate precautions were taken to purify the salt and to keep it pure and dry, many of the earlier determinations of the melting point of sodium nitrite are low. The highest values for the melting point determined[187, 188] are 284°C., and 282°C.[155, 189] for a sample known to be 99·7% pure. Sodium nitrite is known to undergo a transition over the temperature range 160–162°C. accompanied by specific heat changes,[190, 191] a rapid disappearance of the piezo-electric properties of the crystal[191] and changes in the electrical conductivity of the solid.[191] It is also reported that sodium nitrite exists in two crystalline modifications[192] and that above the transition temperature two further crystalline forms exist.[193] The crystal structure of sodium nitrite has been determined.[194–197] The earlier measurements of Ziegler[194] which determined the crystal structure as body-centred orthorhombic (space group C_{2v}^{20}(*Imm*2)) with the unit cell of sides *a* 3·55 A., *b* 5·56 A., and *c* 5·37 A. containing two molecular units have been confirmed[195] although Ziegler's calculated interatomic distances have been criticized.[195–196] Three more recent determinations[195, 196, 197] quote an N–O bond length of 1·23, 1·25 and 1·13, A. and an O–N–O angle of 116°, 114° and 132° 45′ respectively.

The infra-red and Raman spectra of sodium nitrite have been investigated,[198–202] the three expected fundamental frequencies being reported in one investigation[200] to occur at 1328 (A_1), 1261 (B_1) and 828 (A_1) cm.$^{-1}$; the other determinations are in agreement with these. An isotopic shift with $Na^{15}NO_2$ has been noted.[200, 202] It has been stated[198, 199] that a simple valence-force type of potential function is inadequate to describe the observed frequency distribution, but that a more general potential function[200, 202] will do so satisfactorily. The electronic $^1A_1$–$^1B_2$ transition in the ultra-violet has been reported to occur at 28,300[203] and 28,280 cm.$^{-1}$[204] at room temperatures. At low temperatures[201, 202] (77 and 4° abs. respectively) it occurs at 25,960 and 25,977 cm.$^{-1}$ respectively. The value of the extinction coefficient ϵ at room temperature is[203, 204] $\log \epsilon = 1{\cdot}34 \pm 0{\cdot}01$. The irradiation of sodium nitrite at 77° abs. with the 3650–3660 A. mercury arc produces a weak fluorescence[201] analysis of which gives information[201] as to the vibrations of the excited state ($^1B_2$). The ultra-violet absorption of this salt has been used in its quantitative analysis.[205]

Sodium nitrite is very hygroscopic and its stabilization against caking has been the subject of a number of patents.[206–210] One hydrate, $NaNO_2, 0{\cdot}5H_2O$ is known[155, 211] which is formed from solution in the temperature range −19·5 to −5·1°C. with a transition to the anhydrous salt at the higher temperature. The solution of sodium nitrite in water deposits a eutectic containing 28·1% of sodium nitrite at −19·5°C. The solubility diagram for the system sodium nitrite–water[155, 211]

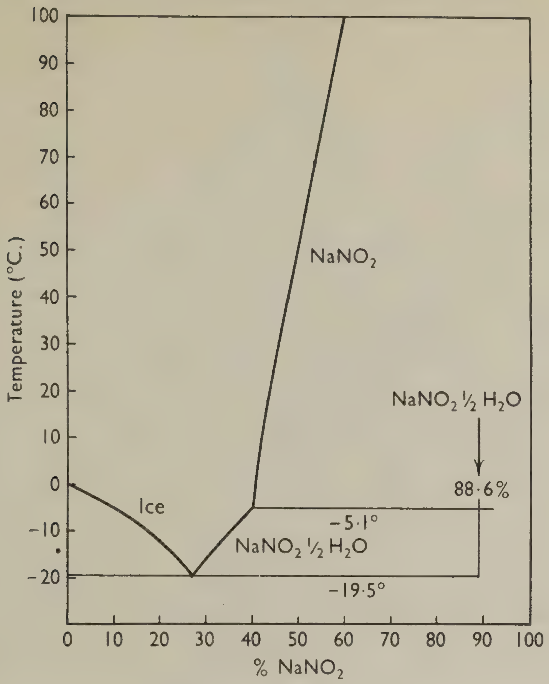

FIG. 3.—The system sodium nitrite–water

is shown in Fig. 3. The freezing points of aqueous solutions of sodium nitrite have been reported.[212]

The solubilities in water of mixtures of sodium nitrite and potassium nitrite have been determined.[213] Solubility diagrams for aqueous solutions of sodium nitrite and sodium nitrate,[214] sodium nitrite and sodium chloride,[214] sodium nitrite and sodium carbonate[215] and sodium nitrite with sodium carbonate and sodium nitrate[215] have been determined and are shown in Figs. 4–7.

The density,[216, 217] refractive index (n_D^{25}),[216] molar conductivity,[216] viscosity[216, 217] and vapour pressures[218, 219] of aqueous sodium nitrite solutions are tabulated in Tables IV–VIII.

Table IV.—Density (g. ml.$^{-1}$) of Aqueous Sodium Nitrite Solutions

<table>
<tr><td></td><td colspan="12">Temperature °C.[217]</td></tr>
<tr><td>Concentration (mole l^{-1})</td><td colspan="2">0°</td><td colspan="2">10°</td><td colspan="2">25°</td><td colspan="2">40°</td><td colspan="2">60°</td><td colspan="2">100°</td></tr>
<tr><td>0·333
0·880
2·860
4·550
6·620
9·610</td><td colspan="2">1·0300
1·0520
1·1290
1·1900
1·2580
1·3160</td><td colspan="2">1·0283
1·0492
1·1268
1·1853
1·2532
1·3113</td><td colspan="2">1·0234
1·0437
1·1179
1·1788
1·2455
1·3043</td><td colspan="2">1·0213
1·0423
1·1149
1·1734
1·2379
1·2982</td><td colspan="2">1·0150
1·0341
1·1066
1·1637
1·2268
1·2821</td><td colspan="2">1·0075
1·0280
1·0830
1·1400
1·2000
1·2570</td></tr>
<tr><td></td><td colspan="12">Temperature 20·1°C.[216]</td></tr>
<tr><td>Concentration (mole l^{-1})</td><td colspan="3">0·5</td><td colspan="3">1·0</td><td colspan="3">2·0</td><td colspan="3">3·0</td></tr>
<tr><td>Density (Mohr scale)</td><td colspan="3">1·0210</td><td colspan="3">1·0427</td><td colspan="3">1·0857</td><td colspan="3">1·1273</td></tr>
</table>

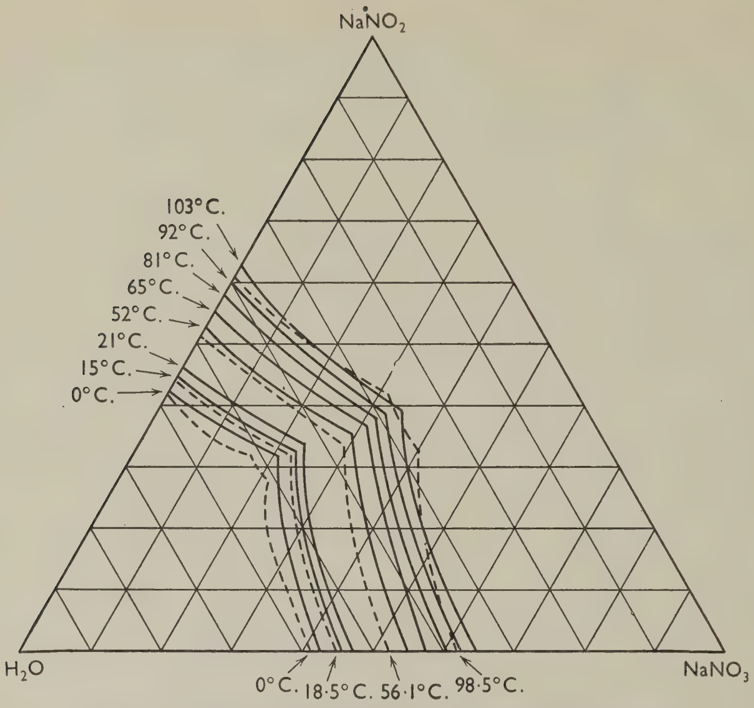

FIG. 4.—The system sodium nitrite–sodium nitrate–water
——— Rakovsky and Slavina[214]
- - - - Bureau[155]

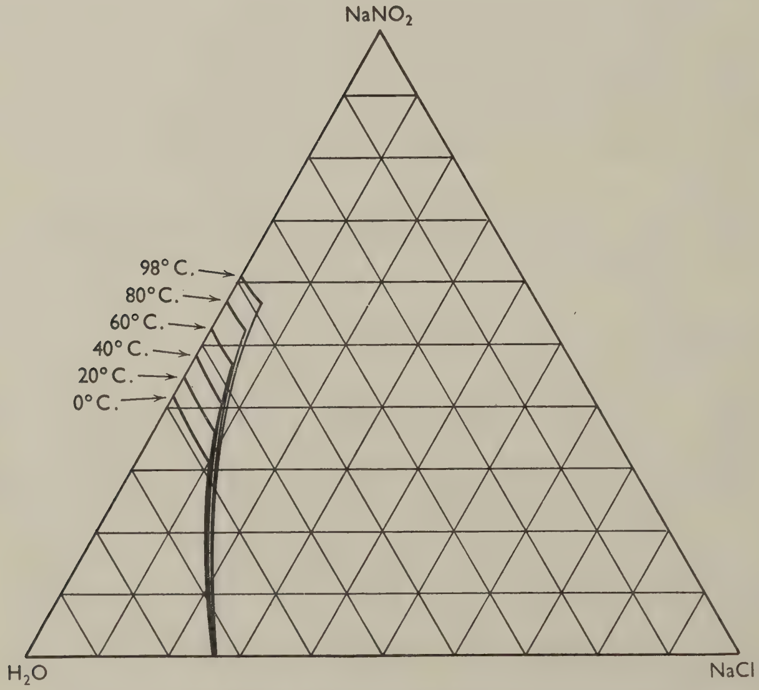

FIG. 5.—The system sodium nitrite–sodium chloride–water

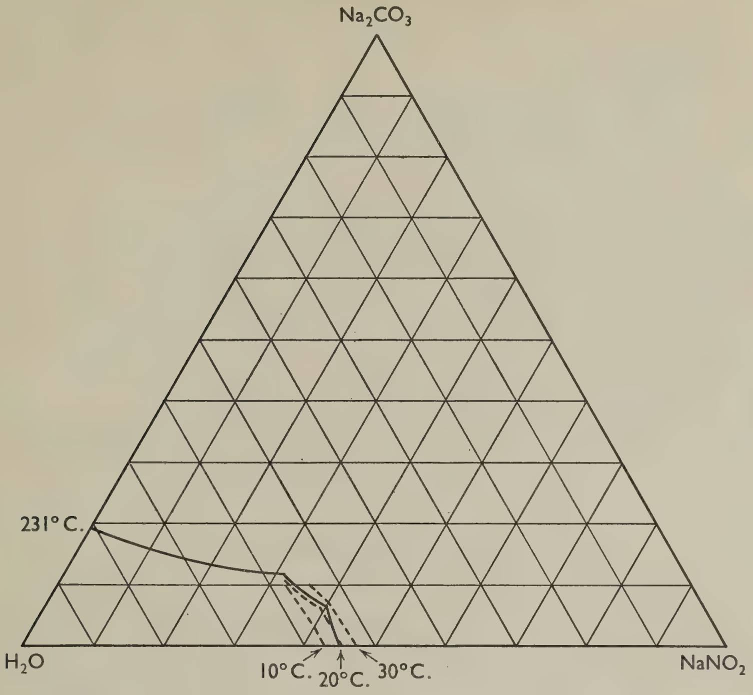

FIG. 6.—The system sodium nitrite–sodium carbonate–water
——— Bureau[155]
– – – – Kuzminykh and Yakhontoya[215]

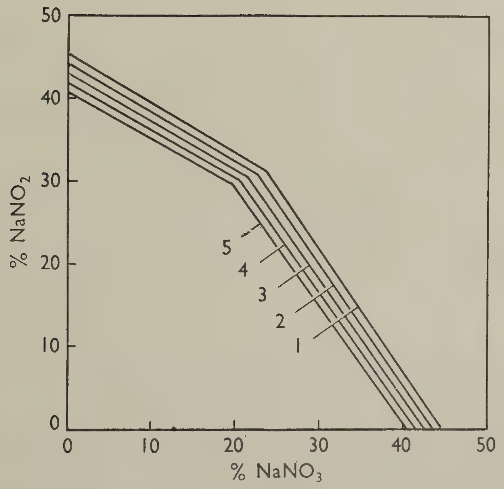

FIG. 7.—Mutual solubility of sodium nitride and nitrate in water when sodium carbonate is present. Temperature 15°C.

Code	1	2	3	4	5
Sodium carbonate	0	1	2	3	4

Table V.—Refractive Index of Aqueous Sodium Nitrite Solutions[216]

Molarity of sodium nitrite	0·5	1·0	2·0	3·0
n_D^{25}	1·3365$_5$	1·3404$_9$	1·3475$_6$	1·3542$_4$

Table VI.—Molar Conductivity of Aqueous Sodium Nitrite Solutions[216]

Molarity of sodium nitrite	0·063	0·125	0·25	0·5
Molar conductivity (mhos mole^{-1})	93·97	82·88	72·36	62·60

The temperature is not quoted; other measurements (density, etc.) were at 20·1°C.

Table VII.—Relative Viscosity (water taken as unity) of Aqueous Sodium Nitrite Solutions[216–217]

	Temperature °C.[217]					
Concentration (mole l^{-1})	0	10	25	40	60	100
0·333	1·0578	1·0505	1·0400	1·0330	1·0250	1·0106
0·880	1·1100	1·0940	1·0690	1·0580	1·0405	1·0310
2·860	1·2530	1·2490	1·1180	1·1912	1·1556	1·1085
4·550	1·5794	1·5420	1·5050	1·4818	1·4398	1·3875
6·620	2·1403	2·1010	2·0132	1·9985	1·9068	1·1772
9·610	3·0414	3·0120	2·6790	2·5400	2·3333	2·1220

	Temperature 20·1°C.[216]			
Concentration (mole l^{-1})	0·5	1·0	2·0	3·0
Relative viscosity	1·006	1·046	1·126	1·281

Table VIII.—Vapour Pressure of Water over Saturated Sodium Nitrite Solutions[218, 219]

Temperature (°C.)	22·8	30·1	37·8	40·0	50·0	60·0	70·0
Vapour pressure (mm. Hg)	13·5	20·16	30·4	33·97	35·30	88·61	137·5
Reference	219	218	219	218	218	218	218

The solubility of sodium nitrite in liquid ammonia has been determined[220] in the temperature range −77·7 to 172°C. and the solubility diagram is shown in Fig. 8. In the temperature range −87·5 to −64·0°C. an ammoniate of formula $2NaNO_2,NH_3$ separates.[220] The electrical conductivity and vapour pressure of such solutions have been measured[220] and the results are given in Tables IX and X respectively.

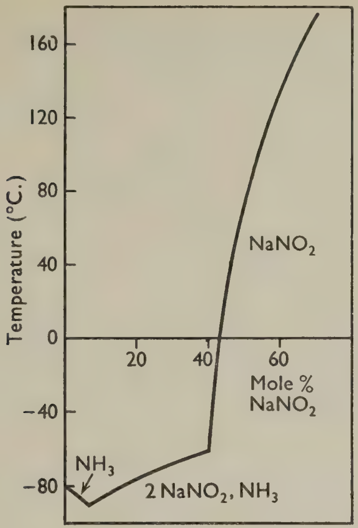

FIG. 8.—The system sodium nitrite–ammonia

Table IX.—Electrical Conductivity of Saturated Solutions of Sodium Nitrite in Liquid Ammonia at Various Temperatures[220]

Temperature (°C.)	−30	−15	−10	+5	15	22·5	25	30·5	40
Electrical conductivity (mhos cm^{-1})	0·1438	0·1723	0·1855	0·2104	0·2197	0·2316	0·2378	0·2500	0·2698

Table X.—Vapour Pressure of Saturated Solutions of Sodium Nitrite in Liquid Ammonia at Various Temperatures[220]

Temperature (°C.)	−27·5	−15·0	−10·0	−5·0	2·5	14·5	16
Vapour pressure (atm.)	1	1·823	2·36	2·94	3·62	4·82	5·31
Temperature (°C.)	17·0	18·0	19·0	28·0	30·0	36·5	
Vapour pressure (atm.)	5·36	5·55	5·65	7·58	7·97	9·98	

Sodium nitrite is slightly soluble in pyridine[221] to the extent of 0·34 g. in 100 g. of solvent at 25°C.

The density of solid sodium nitrite[155] at 0°C. is 2·144 g. cm.$^{-3}$. The heat of solution of sodium nitrite has been reported as −3·57 kcal. mole^{-1} at 20°C.[155] and as −3·66 kcal. mole^{-1} at 14°C.,[222] both investigations using a dilution of 1 g. in 400 ml. water. From the former value[155] the heat of formation of sodium nitrite is estimated as 85·06 kcal. mole^{-1}. The heat capacity of molten sodium nitrite has been measured[189, 223] and the mean heat capacity between the molten sodium nitrite at any temperature and at its melting point is shown as a function of temperature[189] in

Fig. 9. Fig. 9 also shows the mean heat capacity as a function of temperature for a variety of melts[223] of sodium nitrite with sodium nitrate and with both sodium nitrate and potassium nitrate.

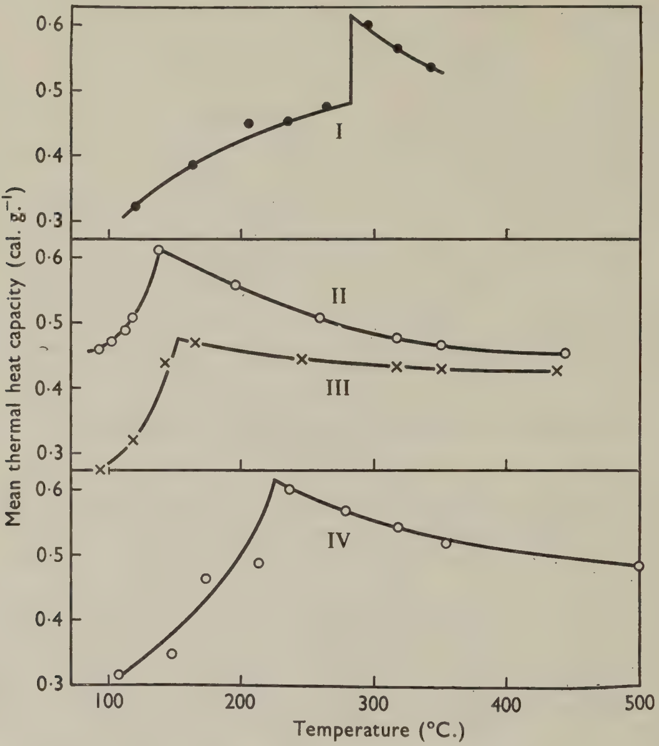

Fig. 9.—Mean heat capacity of fused sodium nitrite (I), 40% sodium nitrite + 53% potassium nitrate + 7% sodium nitrate (II), 28·5%, sodium nitrite + 53·5% potassium nitrate + 18·0% sodium nitrate (III), and 54·9% sodium nitrite + 45·1% sodium nitrate (IV) as a function of temperature

The electrical conductivity of fused sodium nitrite is shown as a function of temperature in Table XI.

Table XI.—Electrical Conductivity of Sodium Nitrite as a Function of Temperature[224]

Temperature (°C.)	433·1	420·0	402·8	383·9	362·7	345·7	331·2
Electrical conductivity (mhos cm^{-1})	2·205	2·121	2·024	1·889	1·787	1·652	1·594
Temperature (°C.)	325·1	307·4	293·0	279·7	272·6	270·2	
Electrical conductivity (mhos cm^{-1})	1·528	1·424	1·331	1·242	1·149	1·114	

The electrical conductivity of fused mixtures of sodium nitrite and potassium nitrate has been recorded.[232]

Numerous fused mixed salt systems having sodium nitrite as one component have been studied. Some results[225] for the system sodium nitrate–sodium nitrite recorded in Figs. 10–13 show the thermal diagram, dependence on molar volume, the molar conductivity and the activation energy for ionic migration as a function of the ole-percentage of sodium nitrate.

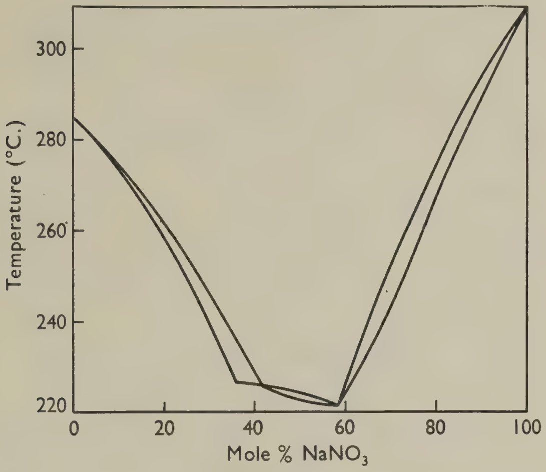

FIG. 10.—Phase diagram for the system sodium nitrite–sodium nitrate

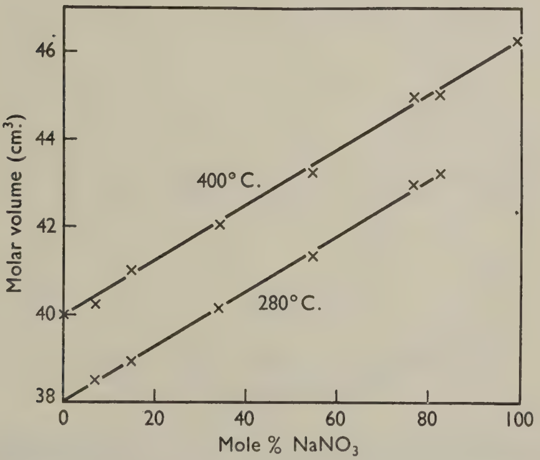

FIG. 11.—Molar volume of the system sodium nitrite–sodium nitrate

Thermal diagrams for mixtures of sodium nitrite with potassium nitrite,[187, 188, 226] with potassium nitrate,[227, 228] with potassium nitrite and potassium nitrate and sodium nitrate,[229] and with potassium nitrate and lithium nitrate[230] are shown in Figs. 14–17. The system sodium nitrite, potassium nitrite, sodium acetate and potassium acetate has also been studied.[231]

The interest in a variety of such melt mixtures having sodium nitrite as one constituent arises from their extensive use as heat-transfer liquids. Such melts have good heat-transfer properties, low melting points and tend to inhibit rather than to cause corrosion such as occurs with other fused electrolytes. The reader is referred to data on two such mixtures reported in the literature: one employs a 50% sodium nitrite, 50% sodium nitrate mixture[233] and the other a mixture of 40% of sodium nitrite, 7% of sodium nitrate and 53% of potassium nitrate.[234–235] The latter mixture has a reported useful temperature range of 150° to 550°C. over which range data

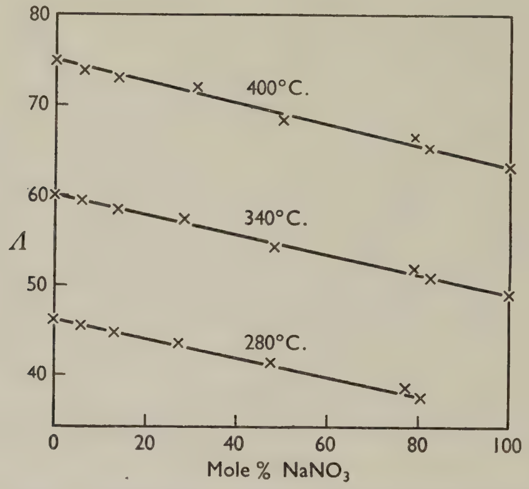

FIG. 12.—Molar conductivity of sodium nitrite–sodium nitrate mixtures

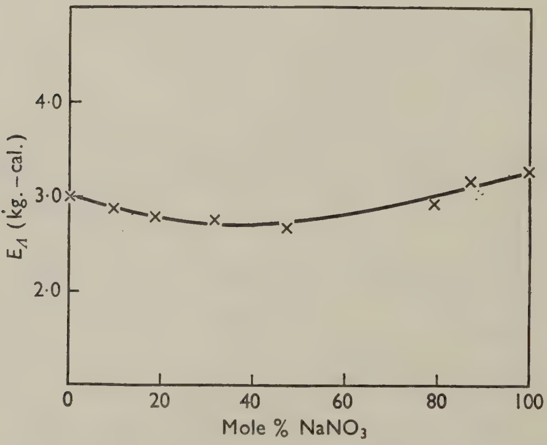

FIG. 13.—Activation energy for ionic migration ($E_Λ$) in the system sodium nitrite–sodium nitrate

such as specific gravity, specific heat, coefficient of heat-transfer and viscosity (the last measured at 440°C.) have been determined.[234]

It is reported[236] that when dry sodium nitrite is fused with sodium monoxide at 300°C. *sodium orthonitrite* is formed. This compound is brown when hot and yellow when cold. An *X*-ray investigation[236] of the product of reaction has shown that the cubic unit cell of side 4·61 A. contains one nitrogen, three oxygen and three sodium atoms and on the basis of these findings the reaction is believed to be:

$$Na_2O + NaNO_2 \rightarrow Na_3NO_3$$

On heating sodium nitrite with sodium azide in vacuo, sodium oxide and nitrogen are produced[237] in practically quantitative yield:

$$3NaN_3 + NaNO_2 \rightarrow 2Na_2O + 5N_2$$

The reaction of nitrogen dioxide with sodium nitrite both at 315°C. and at 450°C. yields the nitrate and nitric oxide. The reaction was found to be practically complete at the higher temperature when the nitrogen dioxide was passed over the nitrite; at the lower temperature a reverse action was detectable, nitric oxide reacting with the sodium nitrate to an extent of 4·5%. Fusion of two moles of urea with one mole of sodium nitrite produces sodium cyanate,[239] but the successful completion of this reaction is extremely dependent on the correct conditions being employed. The procedure is described in great detail[239] and it is reported[239] that other conditions may lead to explosion. Under comparable conditions thiourea gives sodium thiocyanate and guanidine carbonate gives sodium cyanide and sodium cyanate. During

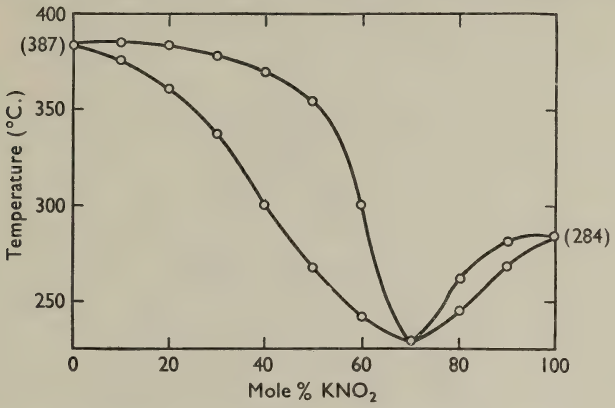

FIG. 14.—Melting and solidification curves for the system sodium nitrite–potassium nitrite

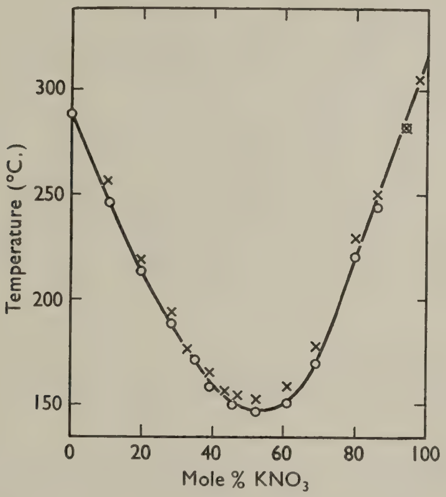

FIG. 15.—Phase diagram of the system sodium nitrite–potassium nitrate. Results of Sakai[228]: x by thermal analysis, o by conductivity measurement. Results of Kagan and Kamuishan[227]:—

the electrolysis of fused sodium nitrite using iron electrodes sodium oxide and nitrogen are formed at the cathode.[240] The primary product formed at the anode is nitrogen dioxide but this immediately oxidizes the nitrite to nitrate until the concentration of nitrate is high enough to allow free nitrogen dioxide to be liberated without further reaction. The electrolysis of a solution of sodium nitrite in liquid ammonia[220] at −35°C. leads to the formation of sodamide and hydrogen at the cathode and of ammonium nitrite and nitrogen at the anode.

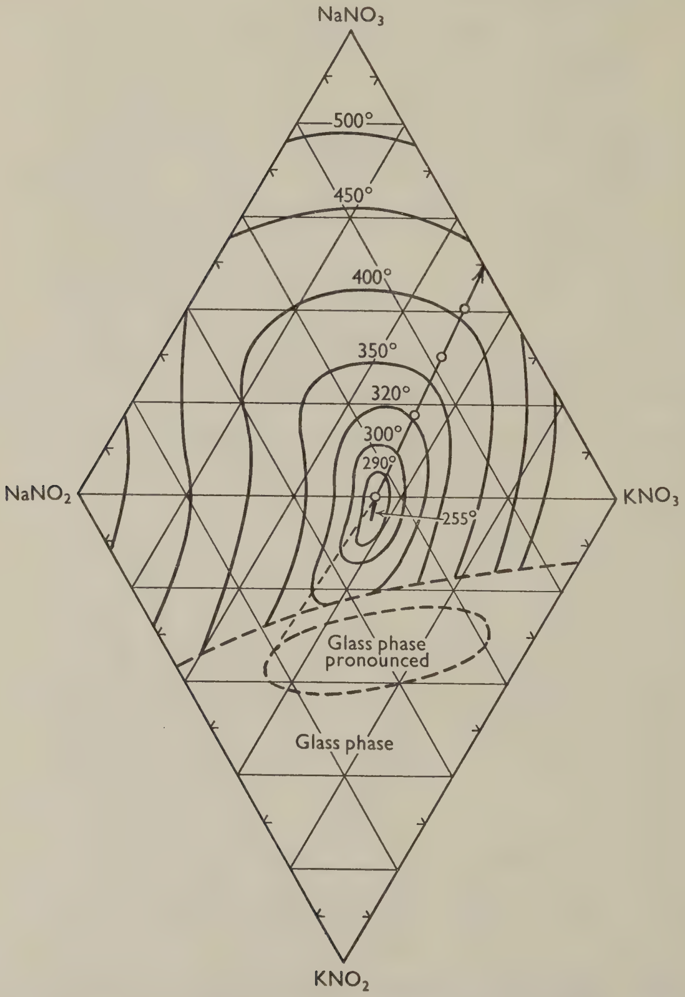

Fig. 16.—Freezing points of alkali nitrate–nitrite mixtures with composition in weight per cent

Sodium nitrite is of considerable industrial importance. Besides its use as a corrosion inhibiter and in the heat-transfer media already referred to, it finds application in the dyeing industry,[241–243] in the curing of meats and fish[244–248] where it is said to be more efficient than sodium nitrate, as a cheap developer,[249] in the production of insulating layers on chromium–nickel wires,[250] as a safety explosive[251] when admixed with potassium ferrocyanide or mercuric cyanide, in the prevention of polymerization during the industrial fractionation of butadiene,[252] in stabilizing vinyl halide resins,[253] as a stopping agent for rubber[254] and in the preparation of many important organic products.

Potassium nitrite has been found as a product when potassium nitrate is reduced with hydrogen under the influence of a 15 kv. silent discharge[255] although potassium hydroxide and ammonia are also formed. In liquid ammonia potassium nitrate can be reduced to the nitrite by means of potassium amide[256] or by metallic potassium,[257] the former reaction being

$$3KNH_2 + 3KNO_3 \rightarrow 3KOH + N_2 + NH_3 + 3KNO_2$$

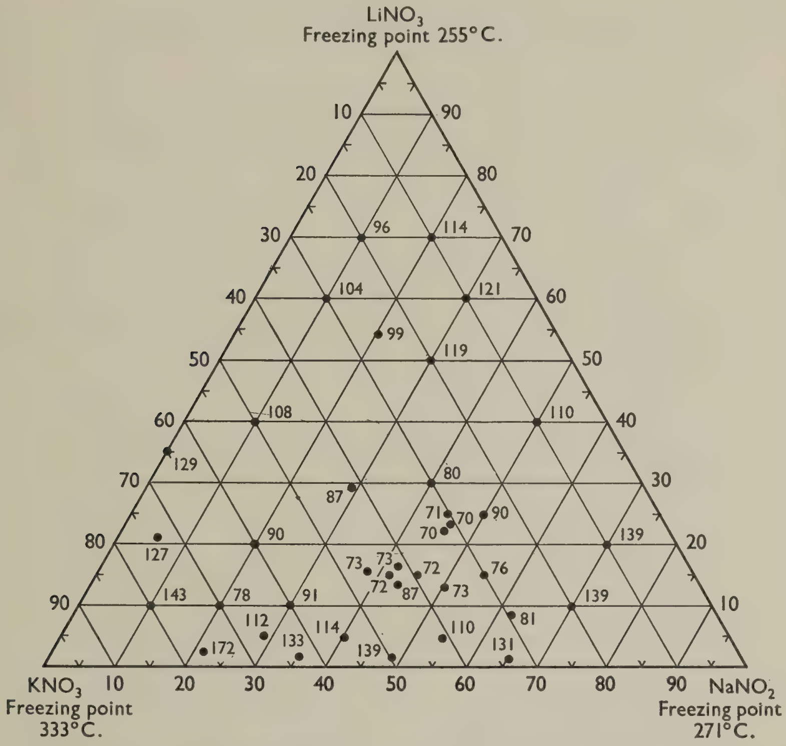

FIG. 17.—Solidification temperatures of mixtures of sodium nitrite–potassium nitrate–lithium nitrate as a function of composition (weight %)

In this reaction, ferric, cobaltic and nickel oxides are extremely effective catalysts, CuO and Mn_3O_4 are fairly effective and even KOH has some catalytic effect making the reaction autocatalytic. The nitrite produced is stated[256] to react extremely slowly with potassium amide as follows:

$$KNO_2 + KNH_2 \rightarrow 2KOH + N_2$$

The reduction with potassium–ammonia solution[257] has been described by the following reaction sequence: (i) $KNO_3 + 2K + NH_3 \rightarrow KNO_2 + KNH_2 + KOH$ followed by (ii) $KNO_2 + K \rightarrow K_2NO_2$ to form *potassium hydronitrite.*

It is reported[258] that when potassium nitrate is heated to 650–700°C., potassium nitrite is formed together with oxygen and nitrogen dioxide, but it is doubtful whether this decomposition can give large yields of potassium nitrite since the nitrite decomposes at these temperatures. At 800°C. the decomposition of the nitrate becomes more extensive as at this temperature the secondary decomposition of the nitrite becomes a major source of oxides of nitrogen.[258] Traces of potassium nitrite are found when mixtures of potassium nitrate and charcoal are heated[259, 260] although the major products are potassium carbonate, carbon dioxide and nitrogen, together with the nitrite decomposition products: potassium oxide, nitrogen dioxide and nitric oxide. The following reactions are believed to occur[259, 260]:

(i) $4KNO_3 + 2C \rightarrow 4KNO_2 + 2CO_2$

(ii) $4KNO_2 + 3C \rightarrow 2K_2CO_3 + CO_2 + 2N_2$

(iii) $KNO_3 + KNO_2 + 2C \rightarrow K_2CO_3 + CO_2 + N_2$

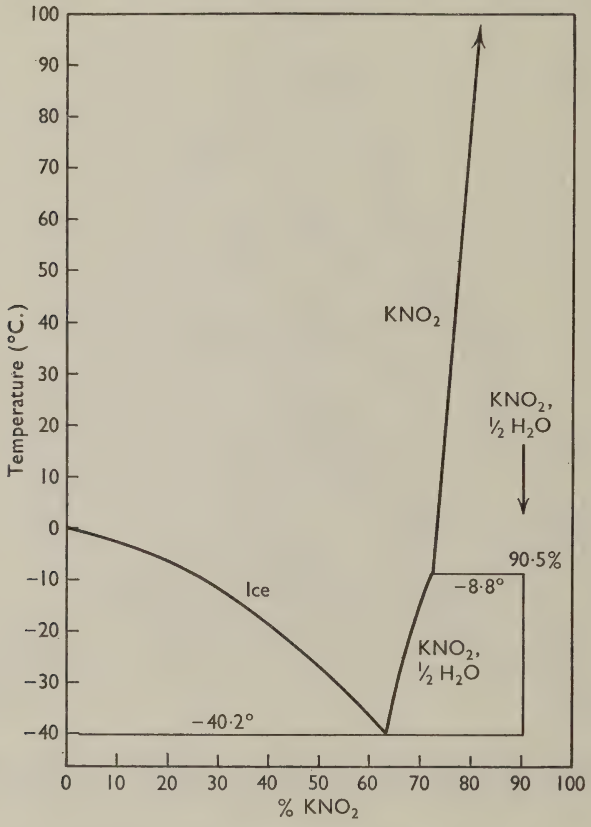

FIG. 18.—The system potassium nitrite–water

The possibility of the laboratory preparation of potassium nitrite by the action of mixtures of nitric oxide and nitrogen dioxide on aqueous potassium hydroxide or potassium nitrite solutions has been investigated[155] under conditions of reaction similar to those described for the preparation of sodium nitrite, but a comparably pure product in practical yield is said[155] to be unobtainable. It has been stated that the purification of potassium nitrite obtained by this method in the laboratory[155] or of industrial samples[186] by recrystallization from water is impracticable as appreciable quantities of carbonate are formed and potassium nitrate and chloride (the latter being present in industrial potassium nitrite) cannot be removed by recrystallization from water. In one instance the isolation of potassium nitrite in the pure state from the commercial substance has been reported[261] to have been successfully accomplished by recrystallization from water. It has been stated,[186] however, that because of the difficulty of purification potassium nitrite is best obtained by the double decomposition of pure silver nitrite and potassium chloride. A pure sample of potassium nitrite has been prepared[155] from an impure starting material (obtained by the absorption of oxides of nitrogen in potassium hydroxide) by recrystallization from boiling 99·5% ethanol, but only in very poor yield. It is reported[262] that crystallization of mixtures of sodium nitrite and potassium chloride gives a product containing between 88·6% and 97% of potassium nitrite. The use of potassium carbonate instead of the chloride[262] yields potassium nitrite of 72% purity. Industrially, potassium nitrite is usually manufactured by the absorption of oxides of nitrogen in aqueous potassium hydroxide or carbonate. As indicated previously, these products may contain much impurity in the form of carbonate, bicarbonate and nitrate and the concentration of these will be increased by exposure to moist air because of the action of atmospheric carbon dioxide (see under sodium nitrite).

The melting point of potassium nitrite as determined by various experimenters shows large variations; this is probably due in many cases to the presence of impurity in the samples used. An analysed pure sample of potassium nitrite has been reported[155] to melt at 441°C. and this is the highest value recorded in the literature. Other values determined[187, 261, 188] are 436°C., 407°C. and 387°C. respectively. An impure sample of 96·5% purity has been stated[263] to melt at 419 ± 3°C. The transition first reported by Bridgman (Mellor, VIII, 474–5) to occur under pressure at a variety of temperatures, has been found[264] to occur at -13 ± 2°C., under 1 atm. pressure with an enthalpy change of $1{\cdot}2 \pm 0{\cdot}2$ kcal. mole^{-1}. An allotropic transformation of potassium nitrite has also been reported[155] to occur at 47°C. The crystal structure of potassium nitrite[179, 265] has a unit cell which is face-centred monoclinic of space group $C^3{}_s(Bm)$ and dimensions a 4·45 A., b 4·99 A., c 7·31 A. and β 114° 50′. The unit cell contains two molecular units. From the X-ray data[265] the N–O bond length has been estimated as 1·14 A. and the O–N–O angle as 132°. The structure may be considered as a distorted sodium nitrite type. The infra-red spectrum of potassium nitrite is similar to that of sodium nitrite.[198, 200] The solubility diagram of the system potassium nitrite–water has been determined[155, 266] and is shown in Fig. 18.

Only one hydrate, $KNO_2,0{\cdot}5H_2O$, is formed and is deposited from solution between $-40{\cdot}2$ and $-8{\cdot}8$°C. There is a transition at $-8{\cdot}8$°C. which corresponds to a solution composition of 71·9% potassium nitrite. At the eutectic temperature of $-40{\cdot}2$°C. the composition is 64·9% potassium nitrite. The three component systems potassium nitrite–sodium nitrite–water,[213] potassium nitrite–potassium nitrate–water,[155, 214] and potassium nitrite–potassium chloride–water[214] have been studied and the phase diagrams of the last two systems are shown in Figs. 19 and 20 respectively.

A phase study of the system potassium nitrite–lead nitrate–water[267] has resulted in the crystallization of the double salts: $4KNO_2,Pb(NO_3)_2$, $2KNO_2,Pb(NO_3)_2$, and $KNO_2,Pb(NO_3)_2$. The density of solid potassium nitrite is reported[155] to be 1·926 g. cm.$^{-3}$ at 0°C. and that of its aqueous solutions at 20°C. is shown[268] as a function of concentration in Table XII.

Table XII.—Density of Aqueous Solutions of Potassium Nitrite[268] at 20°C.

g. KNO_2 in 100 g. water	0	20·0	30·0	40·5	50·0	60·1	65·8	71·9	75·4
Density (g. cm^{-3})	0·9982	1·111	1·192	1·279	1·361	1·467	1·530	1·596	1·635

The surface tension of such solutions is shown in Table XIII.[268]

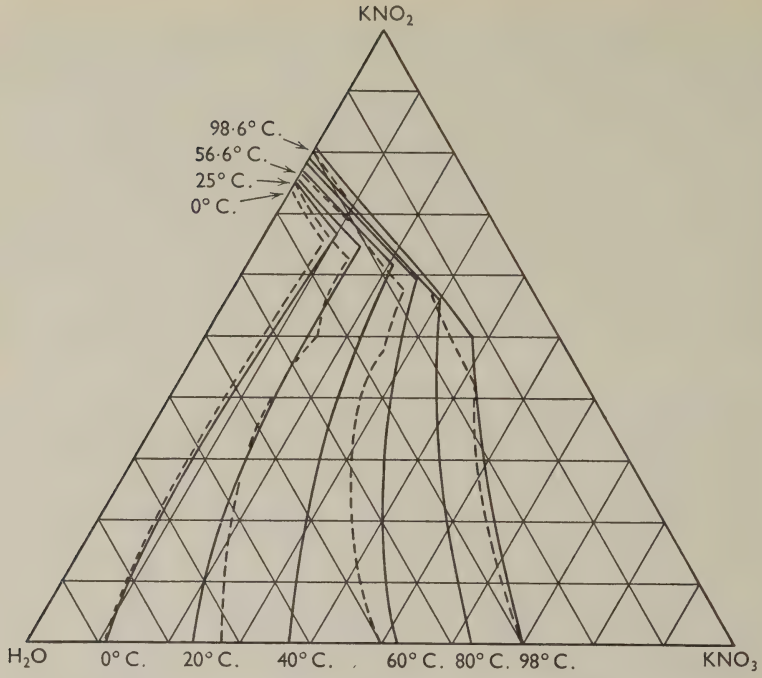

FIG. 19.—The system potassium nitrite–potassium nitrate–water

——— Rakovsky and Slavina[214]

– – – – Bureau[155]

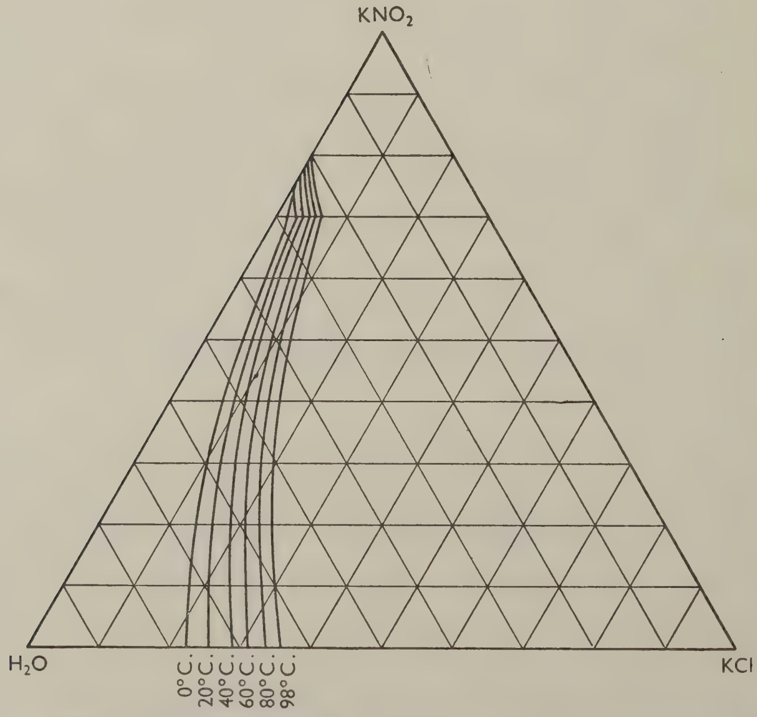

FIG. 20.—The system potassium nitrite–potassium chloride–water

Table XIII.—Surface Tension of Aqueous Solutions of Potassium Nitrite at 20°C.

g. KNO_2 in 100 g. water	0	20·0	30·0	40·5	50·0	60·1	65·8	71·9	75·4
Surface tension (erg cm.$^{-2}$)	72·75	76·0	77·4	79·5	81·7	85·0	88·0	91·7	95·0

Potassium nitrite is practically insoluble in liquid sulphur dioxide.[269] The electrical conductivity of potassium nitrite has been determined[224] as a function of temperature over a temperature range covering the melting point and the results are shown in Table XIV.

Table XIV.—Electrical Conductivity of Potassium Nitrite as a Function of Temperature[224]

Temperature (°C.)	372·0	376·5	380·9	387·4	401·7	411·8
Conductivity (mhos cm.$^{-1}$)	1·094	1·132	1·153	1·191	1·259	1·318
Temperature (°C.)	425·1	445·9	461·9	485·0	508·9	526·9
Conductivity (mhos cm.$^{-1}$)	1·374	1·469	1·514	1·622	1·706	1·778

The melting point diagrams for the systems potassium nitrite–sodium nitrite,[187, 188, 226] potassium nitrite–sodium nitrite–potassium nitrate–sodium nitrate,[229] and potassium nitrite–potassium thiocyanate[270] are shown in Figs. 14, 16, 21, respectively. The last mixture is reported[270] to explode when heated to 400°C. The systems potassium–sodium–nitrite–acetate[231] and potassium–nitrite–nitrate[187] have been investigated.

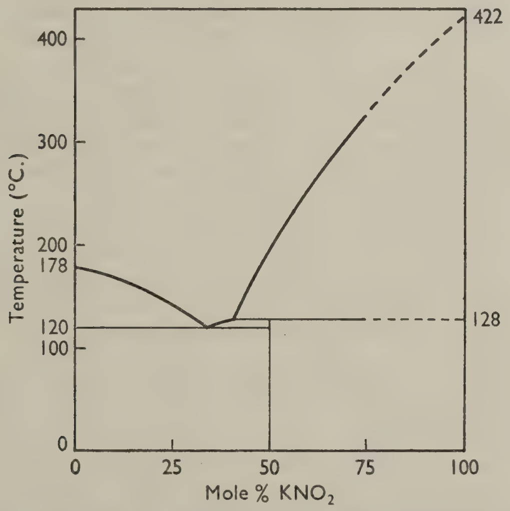

FIG. 21.—Thermal diagram for the system potassium thiocyanate–potassium nitrite

The heat of solution of potassium nitrite in water and the heat of formation of this salt have been determined[155] as −3·40 and 87·66 kcal. mole^{-1} respectively.

It is reported[258] that potassium nitrite can be oxidized by atmospheric oxygen to give potassium nitrate at temperatures 550–600°C. and that this reaction is slow having an activation energy of 34·3 kcal. mole^{-1} and a frequency factor of $10^{3\cdot58}$ sec.$^{-1}$ Rhenium metal is stated[271] to catalyse this oxidation. Potassium nitrite has been catalytically hydrogenated[272] using rhodium, platinum or palladium as catalysts; these metals are given in their order of efficiency at 20°C., but this order is reversed at 50°C. Iodine vapour reacts with potassium nitrite according to the equilibrium[273]:

$$I_2+4KNO_2 \rightleftharpoons 2KNO_3+2KI+2NO$$

which has been studied[273] over the temperature range 300–350°C. Urea reacts with potassium nitrite at elevated temperatures as with sodium nitrite[239] (see p. 381).

The crystal structure of *cæsium nitrite* has been determined.[274] Two crystalline types are reported[274]: a monometric form of cæsium chloride structure (*a* 4·34 A.) and a very fine birefringent needle form which shows a different Debye photograph. It is thought that the existence of the monometric form is evidence that in this structure the nitrite ion is in free rotation.

Ammonium nitrite has been prepared by passing a mixture of nitric oxide and nitrogen dioxide (the concentration of the former being greater) through aqueous ammonia solution.[155] For a successful reaction the solution must be kept cold, replenished with ammonia by passing in a stream of that gas and not allowed to get too concentrated (otherwise the rate of decomposition equals the rate of formation). Evaporation of the end product by means of a stream of air gives a[155] product of 99% purity. In the reaction between ammonia and nitrogen dioxide[275] traces of ammonium nitrite have been found and are believed to be due to a side reaction caused by traces of water.

Ammonium nitrite is unstable, decomposing according to the overall reaction:

$$NH_4NO_2 \rightarrow 2H_2O+N_2$$

This reaction can be explosive in the solid state; a mixture of sodium nitrite and ammonium chloride is a commercial explosive, 'Hydrox', depending for its effect upon the formation of ammonium nitrite. It has[276] a heat of explosion of 52·4 kcal. mole^{-1}, an explosion temperature of 1430°C. and produces 540 l. of gas per kg. of explosive at N.T.P. The kinetics and mechanism of the decomposition of ammonium nitrite in solution (which is identical with the reaction of nitrous acid and ammonia in aqueous solution) have been studied.[277–280] The reaction is acid catalysed and one investigator[277] postulated the formation of the short-lived N_2H^+ ion as an intermediate. In general terms the reaction is now believed to proceed by the following sequence[278] when the solution is only weakly acidified:

$$NH_4NO_2 \rightarrow NH_4{}^+ + NO_2{}^-$$
$$NH_4{}^+ \rightarrow NH_3+H^+$$
$$2H^+ + NO_2{}^- \rightarrow H_2ONO^+ \text{ (or } H_2O+NO^+)$$

followed by the rate-determining step:

$$NO^+ + NH_3 \rightarrow NH_3NO^+$$

and finally by decomposition:

$$NH_3NO^+ \rightarrow N_2+H^+ + H_2O$$

It is to be noted that the suggested intermediate NH_3NO^+ ion may be considered as a solvated N_2H^+ ion. It has been found[278] that the reaction is not generally acid catalysed, but that in strong hydrogen halide solutions there is evidence[279] for the participation of nitrosyl halide:

$$HNO_2+HX \rightleftharpoons NOX+H_2O$$
$$NH_4{}^+ \rightleftharpoons NH_3+H^+$$

followed by the rate-determining step:

$$NH_3 + NOX \rightarrow NH_2NO + H^+ + X^-$$
$$NH_2NO \rightarrow HN_2OH \rightarrow HN_2^+ + OH^-$$
$$HN_2^+ \rightarrow N_2 + H^+$$
$$H^+ + OH^- \rightarrow H_2O$$

During the course of the reaction a trace of nitrate has been found[280] and this is believed to be due to atmospheric oxidation. In applying this reaction to the gasometric analysis of nitrites or ammonium salts,[281] it is carried out in boiling solution and the evolved nitrogen is determined. In this manner $^{15}N_2$ has been isolated for isotope analysis.[282]

Copper nitrites. Neither cuprous nor cupric nitrite is known in the free solid state. The basic nitrite $Cu(NO_2)_2,CuO$ has been described[283, 284] and is reported[284] to be formed by the decomposition of the $Cu(NO_2)_6{}^{4-}$ ion formed[284] during electrolysis of aqueous solutions of sodium nitrite with a copper anode. The addition of nitrite ion to a cupric ion solution results in the formation of a series of complex nitrites of copper; such solutions, which are green in colour owing to complex formation, have been investigated.[283, 285–287] The following equilibria are usually thought to occur:

(i) $Cu^{++} + NO_2^- \rightleftharpoons CuNO_2^+$

(ii) $CuNO_2^+ + NO_2^- \rightleftharpoons Cu(NO_2)_2$

(iii) $Cu(NO_2)_2 + NO_2^- \rightleftharpoons Cu(NO_2)_3^-$

and, less well established,

(iv) $Cu(NO_2)_3^- + NO_2^- \rightleftharpoons Cu(NO_2)_4^{2-}$

The equilibrium constants for these reactions, which appear to be very dependent on the ionic strength,[286] have been found[286, 287] to have values at 25°C. in the range 16 to 20 l. mole^{-1} for the first equilibrium, 1·7 to 2·3 l. mole^{-1} for the second equilibrium and 0·4 to 0·2 l. mole^{-1} for the third equilibrium. These results show that it is more difficult to attach each successive nitrite group to the complexes. There is a strong probability[285] that the copper co-ordination number is made up by ligand water molecules. The solid triple nitrite complexes of copper of general formula $M_2{}^IM^{II}[Cu(NO_2)_6]$ (where M^I is K, NH_4, Rb, Cs or Tl and M^{II} is Ca, Sr, Ba or Pb) (Mellor, VIII, 488 and 498) have been further studied. Their preparation with special regard to their interrelation has been described[288] including the first preparation of the cæsium and rubidium members.The thallium members have also been described.[289] The complex $K_2Pb[Cu(NO_2)_6]$ has been adapted to the quantitative determination of potassium,[290] the complex being formed *in situ.* Magnetic measurements on the members $K_2Ca[Cu(NO_2)_6]$ and $(NH_4)_2Pb[(Cu(NO_2)_6]$[291] indicate that these are complexes of the hexanitrocopper (II) anion. Structurally[292] these compounds have a cubic unit cell of space group $T_h{}^3(Fm3)$. The complex previously held to be $K_3Cu(NO_2)_5$ has been shown[288] to be $K_3[Cu(NO_2)_5H_2O]$.

When thallous nitrite reacts with basic copper acetate the solution changes colour from blue to yellow-green[289]; evaporation of the product in vacuo over strong sulphuric acid yields opaque black crystals of *thallous cupric nitrite*, $Tl_3[Cu(NO_2)_5]$. This salt and its aqueous solutions are[289] stable at ordinary temperatures. *Di-pyridinocupric nitrite*, $[Cu(C_5H_5N)_2](NO_2)_2$ has been prepared[293] by reacting equal volumes of pyridine and a green solution obtained when 1 mole of cupric sulphate is mixed with 2 moles of potassium nitrite in water and freed from potassium sulphate and copper hydroxide by precipitating these with an equal volume of ethanol. Greenish-black monoclinic prisms are formed[293]; m.p. (decomp.) 155°C. Treatment of the same copper–nitrite solution with aniline, *p*-toluidine or *β*-naphthylamine yields the corresponding *di-arylaminecopper* (II) *nitrites.* If to a solution of sodium nitrite (10 g.) and cupric sulphate (9 g.) in 50 ml. of water at 0°C., thiourea

(3·8 g. in 50 ml. of water at 0°C.) is rapidly added with agitation, a yellowish compound is precipitated which may be filtered, washed with ice water and dried in vacuo.[294] It has the composition[294] $CuNO_2,SC(NH_2)_2,0{\cdot}5H_2O$ and the probable structure $[CuSC(NH_2)_2.(NO_2)_2][CuSC(NH_2)_2H_2O]$. This, by the action of cold dilute hydrochloric acid in the absence of air,[294] yields the compound $CuCl.SC(NH_2)_2.Cu(NO_2)SC(NH_2)_2,0{\cdot}5H_2O$. The compound $[Cu(SCN_2H_4)_3(NO_2)_2][CuSCN_2H_4.H_2O]$ has also been prepared[294] by the action of sodium nitrite (1 g.) on $Cu(SC(NH_2)_2)_3Cl$ (3 g.) in water. This compound is also produced[294] by dissolving $[Cu(SCN_2H_4)Cl_2][Cu(SCN_2H_4)H_2O]$ in aqueous thiourea and adding sodium nitrite, but if the solution is allowed to stand $[Cu(SCN_2H_4)_2H_2O]NO_2$ results. If the compound $CuNO_2SCN_2H_4,0{\cdot}5H_2O$ described above is dissolved in aqueous thiourea and sodium nitrite is added the precipitate formed is the compound $[Cu(SCN_2H_4)H_2O]NO_2$[294]: water decomposes this immediately to form $CuNO_2SCN_2H_4,0{\cdot}5H_2O$.

Silver nitrite is formed[181, 255] when hydrogen in contact with silver nitrate is subjected to a high tension discharge. It has also been found[295] after a glow discharge has been occurring between silver electrodes in air. Silver nitrite, which is an important laboratory intermediate in the preparation of other nitrites and nitro compounds, is usually prepared by precipitating an aqueous solution of silver nitrate with sodium nitrite and filtering off the sparingly soluble silver nitrite. The use of pure starting materials and the washing of the product ensure purity.

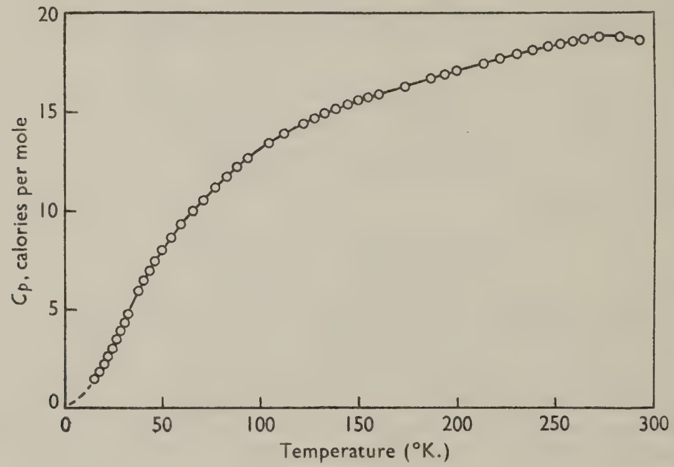

FIG. 22.—Molal heat capacity of silver nitrite as a function of temperature

The structure of silver nitrite has been determined[296, 297]: it has an orthorhombic space group, C_{2v}^{20}(*Imm*2) with a unit cell of sides *a* 3·505 ± 0·007 A., *b* 6·14 ± 0·01 A., *c* 5·16 ± 0·02 A. containing two structural units.[297] The molecule is silver–nitrogen linked.[297] The molal heat capacity of silver nitrite has been measured[298] in the temperature range 15 to 300° Abs. and the values are shown graphically in Fig. 22. The entropy and heat of solution at infinite dilution have been determined[298] at 298·1° Abs. as 30·62 e.u. and 10·07 ± 0·1 kcal. mole^{-1}. The latter value was calculated as the sum of the heat of solution at infinite dilutions of silver nitrite in ammonia and of silver nitrate in water minus the value for silver nitrate in ammonia at infinite dilution. Under the influence of 3650 A. mercury light and at temperatures below 90°C. silver nitrite fluoresces.[299–301] At the higher temperatures (room) the fluorescence is red and moderately strong, improving in intensity and becoming greenish-yellow at liquid oxygen temperatures.[299] The spectrum at these low temperatures[300] shows five bands separated by about 750 cm.$^{-1}$ in the frequency range 16,080 to

19,080 cm.$^{-1}$; these separations are thought,[300] by comparison with the infra-red spectrum, to be due to vibrations of the nitrite ion. Lattices made up of sodium nitrite containing 10 mole-% of silver nitrite and silver nitrite containing 10 mole-% of sodium nitrite also fluoresce.[300] It is therefore concluded[300] that the silver and nitrite ions do not need to be there abundantly as a silver nitrite lattice, but rather that discrete silver nitrite pairs are required; mechanistically it is believed[300] that the covalent silver nitrite molecule acts as a lattice defect in the ionic structure and that the electrons emitted by photo-excitation are temporarily trapped in this defect, later returning into the lattice and thereby emitting energy in the form of fluorescent light. In saturated aqueous solution, silver nitrite on exposure to a mercury arc radiation is decomposed[302] with the formation of metallic silver and nitrogen dioxide. The reaction has been found[302] to be monomolecular with an effective radiation wave-length range of 2800 to 3135 A. and a quantum efficiency of the order of 10^8. This quantum efficiency is said[302] to vary with the nature of the glass.

The thermal decomposition of silver nitrite is said[303] to depend on two equilibria:

(i) $AgNO_2 \rightleftharpoons Ag + NO_2$

(ii) $AgNO_2 + NO_2 \rightleftharpoons AgNO_3 + NO$

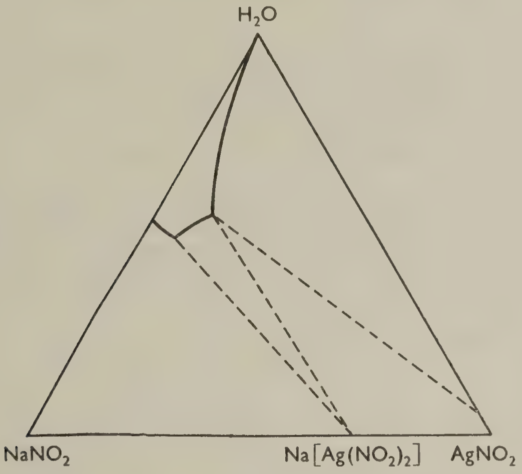

FIG. 23.—The system sodium nitrite–silver nitrite–water at 25°C

The equilibrium between silver nitrate, silver nitrite, silver and nitric oxide has been measured[156] in the temperature range 101·6 to 149·0°C. and the thermodynamic functions $\Delta G°$, $\Delta H°$ and $\Delta S°$ were calculated to have the values 3·55 ± 0·01 kcal., 13·39 ± 0·03 kcal. and 32·03 ± 0·05 e.u. respectively at 298·1° Abs.

The systems sodium nitrite–silver nitrite–water[304] and potassium nitrite–silver nitrite–water[305] have been investigated and their solubility diagrams are shown in Figs. 23 and 24 respectively.

The salt $NaAg(NO_2)_2$ crystallizes from aqueous solutions of silver nitrite and sodium nitrite containing relatively high concentrations of sodium nitrite; it is a pale yellow compound belonging crystallographically[304] to the orthorhombic system (space group either D_{2h}^{20} (*Cccm*) or C_{2v}^{13} (*Ccc*2) of unit cell sides *a* 7·89 ± 0·01 A., *b* 10·62 ± 0·03 A., and *c* 10·83 ± 0·01 A. containing 8 molecular units. The equilibrium constant for the reaction:

$$AgNO_2 + NO_2^- \rightleftharpoons Ag(NO_2)_2^-$$

calculated[306] from solubility data for silver nitrite in nitrite solutions, is 0·0521 ± 0·0011 l. mole^{-1} at 25°C. From this value and the data of Abegg and Pick (Mellor,

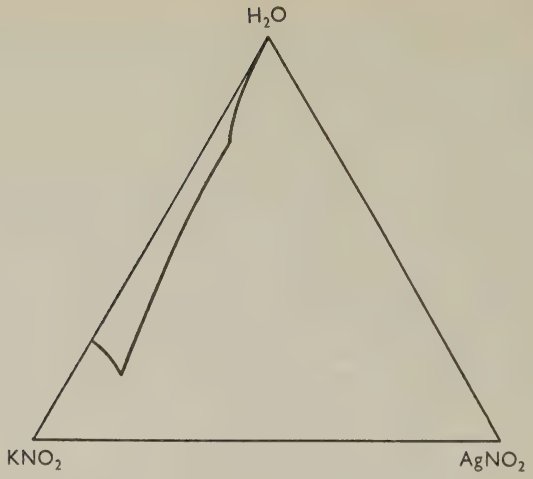

FIG. 24.—The system potassium nitrite–silver nitrite–water 27°C

VIII, 482) on the solubility of silver nitrite in water, it is estimated[306] that the solubility product of silver nitrite at 25°C. is $1{\cdot}5\times10^{-4}$ $l.^2$ $mole^{-2}$, and that the equilibrium constant for the reaction

$$AgNO_2\ (soln.) \rightleftharpoons Ag^+ + NO_2^-$$

is $1{\cdot}5\times10^{-2}$ l. $mole^{-1}$ at 25°C. The stability of the undissociated molecule is attributed[306] to the covalent bonding between the silver and nitrogen of the nitrite ion. The salt sodium silver nitrite has also been formed by the electrolysis of sodium nitrite with a silver anode.[307] An anolyte of 50 g. of sodium nitrite in 100 ml. of

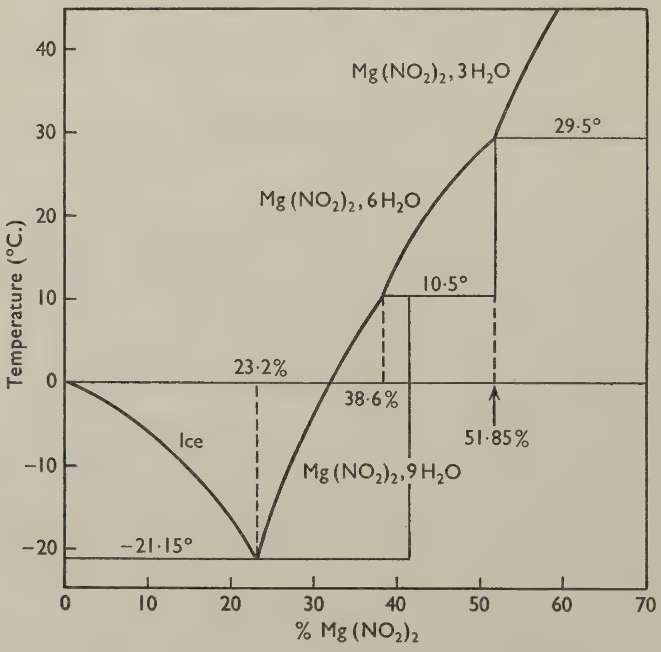

FIG. 25.—The system magnesium nitrite–water

water was used and current at a density of 0·761 × 10^{-3} amp. $cm.^{-2}$ was passed for 55 hours. No oxygen was evolved. Evaporation of the resulting anolyte in a vacuum desiccator over concentrated sulphuric acid produced well-formed crystals of sodium silver nitrite.

Attempts to prepare *beryllium nitrite*[155, 283] have been unsuccessful; the nitrite appears to be too unstable to exist at room temperature even in dilute aqueous solution, and such solutions decompose to give beryllium oxide and oxides of nitrogen.

Magnesium nitrite has been prepared by the absorption of a mixture of nitric oxide (in slight excess) and nitrogen dioxide into a suspension of magnesium hydroxide in water.[155, 308] The product is contaminated with nitrate. Double decomposition of magnesium chloride and silver nitrite has also been used to prepare magnesium nitrite[153, 307] and the product, $Mg(NO_2)_2,9H_2O$, is separated[308] by cooling the aqueous filtrate after reaction, rather than by evaporation under reduced pressure, since it was found[308] that on evaporation extensive decomposition of the nitrite occurred when the concentration of the solution reached 45%. Alternatively the solution could be evaporated over phosphorus pentoxide to yield a hydrate described variously as containing two[153] or three[308] moles of water. The solubility diagram of the system magnesium nitrite–water[308] is shown in Fig. 25.

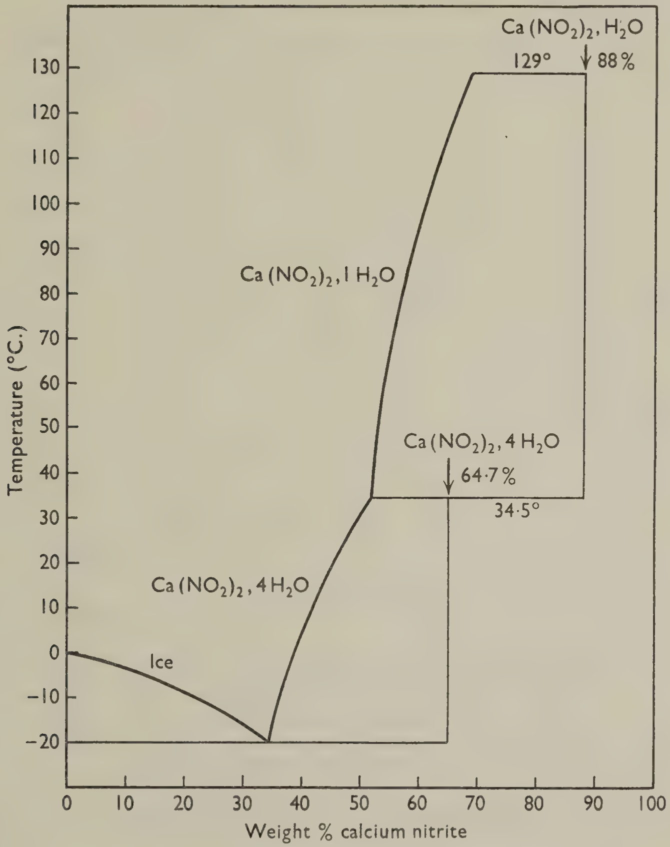

FIG. 26.—The system calcium nitrite–water

The system has a eutectic point at −21·15°C., the eutectic containing 23·2% $Mg(NO_2)_2$ as the nonahydrate.[308] In solution at 10·5°C. there is a transition to the hexahydrate and at 29·5°C. a further transition leads to the tri- (or di-[153]) hydrate.[308] In the solid state[308] the nonahydrate is transformed into the hexahydrate at 12°C. and the latter is stable up to 34°C.

Calcium nitrite has been found as a reaction product when hydrogen in contact with calcium nitrate is subjected to a high-voltage electric discharge.[181] The reaction of calcium nitrate with nitric oxide and calcium ferrate at 275°C. for 48 hours in a vacuum system (see sodium nitrite) is reported[185] to give 99% pure calcium nitrite. Calcium nitrite has been prepared[309] by the reaction of silver nitrite with an ammoniacal solution of calcium chloride. An industrial technique reputed to give 99·3% yield of calcium nitrite by the absorption of mixtures of nitric oxide and nitrogen dioxide in aqueous calcium hydroxide has been described,[310] but the work of Bureau[155] indicates that this method would lead to an impure product which is difficult to purify.

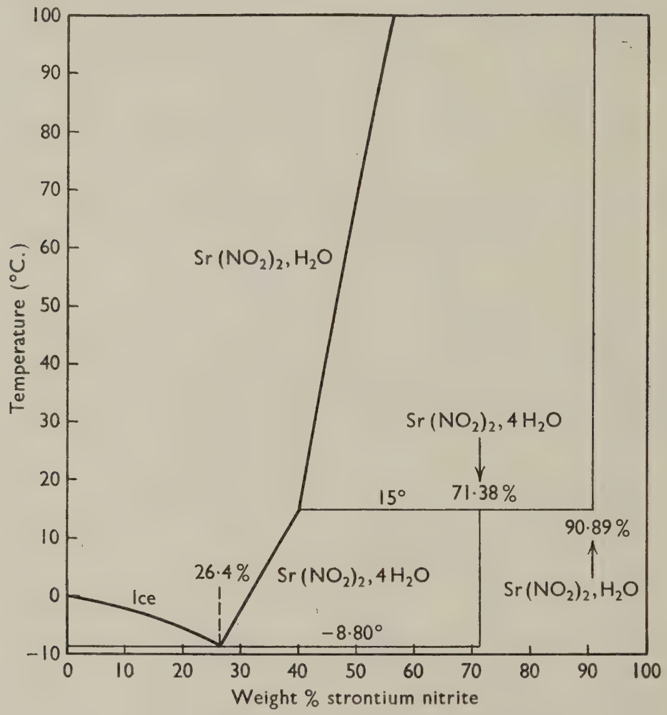

FIG. 27.—The system strontium nitrite–water

The solubility diagram for the system calcium nitrite–water[155, 311] is given in Fig. 26.

Two hydrates are formed,[155, 311] a mono- and a tetra-hydrate, the latter being stable below 34·6°C. at which temperature there is a transition to the monohydrate which is stable up to 129°C., but above this temperature loses water. From solution a eutectic is formed at −20°C. which contains 34·2% of calcium nitrite.[311] It has been reported[155] that calcium nitrite undergoes an allotropic transformation at 138°C. The heats of solution and formation of calcium nitrite have been determined[155] and have the values −2·04 kcal. mole^{-1} and 184·26 kcal. mole^{-1} respectively. A *basic* calcium nitrite, $Ca(OH)_2,Ca(NO_2)_2,2H_2O$, has been reported[312] to be formed when warm solutions of calcium nitrite are treated with calcium oxide.

Strontium nitrite can be obtained[155] by the action of nitric oxide (in slight excess) and nitrogen dioxide on an aqueous suspension of strontium hydroxide, although the product is not of the highest purity. The salt has been prepared[309] by the action of silver nitrite on an ammoniacal solution of strontium chloride. The solubility diagram for the system strontium nitrite–water[155, 313] is shown in Fig. 27.

The salt exists in two hydrated forms,[155, 313] $Sr(NO_2)_2,H_2O$ and $Sr(NO_2)_2,4H_2O$, the latter being stable below 15°C. at which temperature there is a transition to the monohydrate. The anhydrous salt melts[155, 313] with decomposition at 276°C. From aqueous solution a eutectic is formed at $-8{\cdot}7$°C. containing 26·4% of strontium nitrite.[313] The heats of solution and formation are 2·04 kcal. mole^{-1} and 184·96 kcal. mole^{-1} respectively.[155] This salt is extremely hygroscopic and for this reason it has not been feasible to obtain suitable *X*-ray photographs for a structural analysis to be attempted.[314]

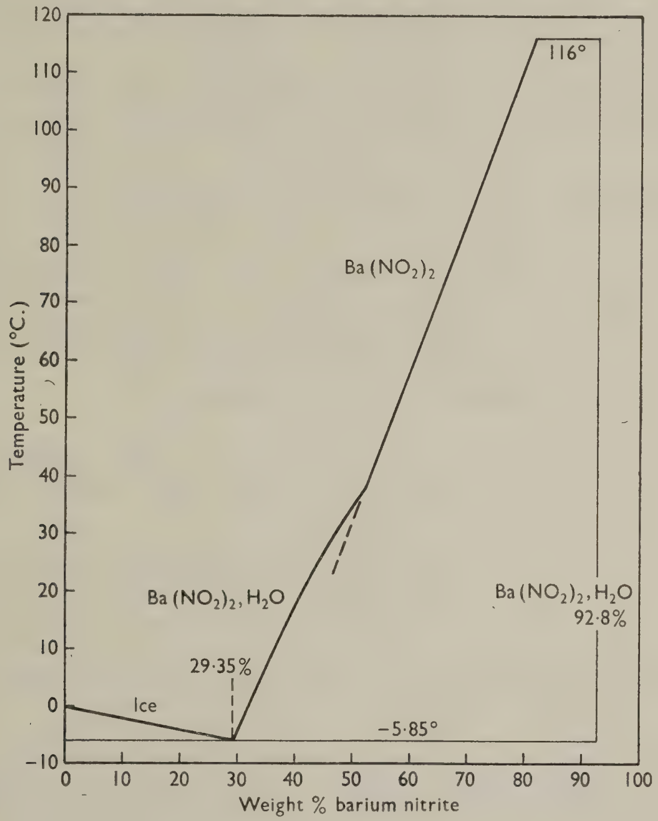

FIG. 28.—The system barium nitrite–water

Barium nitrite can be successfully prepared by the absorption of mixtures of nitric oxide (in slight excess) and nitrogen dioxide by aqueous baryta until the solution is just neutral to phenolphthalein.[155] Impurity in the form of carbonate, hydroxide and nitrate is easily removed by simple recrystallization.[155] This nitrite has also been prepared by the action of silver nitrite on ammoniacal barium chloride.[309] *X*-Ray diffraction patterns of barium nitrite monohydrate indicate that[314] the crystals are hexagonal (space group D_6^2 ($P6_122$) or D_6^3 ($P6_522$)) of side *a* 7·05 A., *b* 17·66 A., the orthorhombic unit cell containing six structural units. Further analysis has elucidated the barium ion positions. The fact that there is no change in the *X*-ray powder photograph when the nitrite is heated to 100°C. and loses water is held to indicate[314] that the water of crystallization is zeolitic in character. The solubility diagram of aqueous barium nitrite[155, 313] is shown in Fig. 28.

The salt is said[155, 313] to exist with 1 molecule of water of crystallization but to have two crystalline modifications: a hexagonal form stable to 40°C. and a rhombic form above this temperature. The aqueous solution deposits a eutectic at $-5{\cdot}8$°C. containing 20·3% of barium nitrite.[313] The salt dehydrates[313] at 116°C. and melts[313] at 267°C. with slight decomposition. Two allotropic transformations are reported[155] to occur, one at 20°C. and the other at 231°C. The heats of solution and formation[155] are $-5{\cdot}56$ kcal. mole^{-1} and 183·05 kcal. mole^{-1} respectively.

Barium nitrite reacts with iodine at elevated temperatures and the reaction has been studied[315] at 235°C. when the following equilibrium is formed:

$$2Ba(NO_2)_2+I_2 \rightleftharpoons Ba(NO_3)_2+BaI_2+2NO$$

A mixture of 72% (by weight) of barium nitrite and 28% (by weight) of sodium cyanide has been patented[251] as a safety explosive which can be detonated by heating or by a primer.

Cadmium nitrite. It is believed[283] that solutions of cadmium cations and nitrite anions exist as a mixture of the $[Cd(NO_2)_3]^-$ and $[Cd(NO_2)_4]^{2-}$ ions, the former probably having a single water molecule as ligand to make up the co-ordination number of four. The dissociation constants of these ions are less than for the corresponding mercury salts and greater than for the corresponding lead salts.[283] Di-hydrazine cadmium (II) nitrite, $[Cd(N_2H_4)_2](NO_2)_2$,[316] is a white compound which detonates on heating or when treated with concentrated sulphuric acid or nitric acid. Dilute acids react with it to give nitrogen and nitrous oxide.[316]

Mercury nitrite. The complex ion $[Hg(NO_2)_4]^{2-}$ is[283] formed when mercuric and nitrite ions are mixed in aqueous solution; this complex is more stable than the corresponding cadmium compound.[283] The equilibrium constant for the reaction:

$$Hg(NO_2)_2+Zn(NO_2)_2 \rightleftharpoons Zn[Hg(NO_2)_4]$$

is $0{\cdot}53\pm0{\cdot}03$ l. mole^{-1}.

Aluminium nitrite is said[318] to be formed as a transient product during the electrolysis of sodium nitrite with an aluminium anode, but the product could not be isolated because of hydrolysis to the hydroxide.

Yttrium nitrite is unknown, but a green compound $Cs_2Na[Y(NO_2)_6]$ has been prepared[319] by diffusing an aqueous solution of cæsium nitrate through a parchment membrane into a solution of yttrium nitrate and sodium nitrite: the optimum ratio for the concentrations of cæsium, yttrium and nitrite was 2:1:9. *X*-Ray analysis shows[319] that this complex has a cubic unit cell of space group T_h^3 (*Fm*3), of side a $11{\cdot}06\pm0{\cdot}01$ A., containing 4 molecular units. It has been suggested that the bonds between the co-ordinated yttrium ion and the nitrite ions are ionic.[319]

A basic *lanthanum nitrite*, La_2O_3,N_2O_3, has been reported.[320] It is stated[320] that this compound can be obtained when solutions of lanthanum chloride and sodium nitrite are mixed at pH 5, the nitrite solution being 0·5 to 2·0 molar. Weaker solutions result in the precipitation of lanthanum hydroxide.[320] The pale green complex $Cs_2Na[La(NO_2)_6]$ has been prepared[319] from lanthanum nitrate by a method exactly similar to that employed for the preparation of the yttrium complex. It is isometric with the yttrium complex[319] having a cubic unit cell containing 4 molecular units and of side $11{\cdot}24\pm0{\cdot}01$ A.

Similar complexes of *cerium* (canary yellow) and *praseodymium* (pale green) have also been prepared[319] by the same method. These two salts are isometric with the yttrium salt and have a cubic unit cell containing 4 molecular units and of side $11{\cdot}20\pm0{\cdot}01$ A. and $11{\cdot}18\pm0{\cdot}01$ A. respectively.[319]

Thallous nitrite is prepared[321] as a light orange solid by the action of thallous sulphate on barium nitrite, followed by evaporation of the filtrate at 80°C. *Thallic nitrite* is formed[322] in aqueous solution by the reaction of thallic sulphate on barium nitrite, but attempts[322] to obtain it in the solid state from these solutions, even at low temperatures, have failed owing to the extensive decomposition that occurs. Attempts[322] to prepare thallic nitrite by the action of nitric oxide and nitrogen dioxide on an aqueous suspension of thallic oxide fail: thallic nitrate is formed as the product. It has been stated[322] that thallic nitrite is much more stable in ethereal solution and that from such a solution a salt believed to be the impure nitrite was obtained[322] on evaporating the ether, but no successful analysis of the deposited salt was reported.[322] The melting point of thallous nitrite is reported[323] as 182°C. The ionic dissociation constant of thallous nitrite determined[324] by electrical conductivity measurements is 0·16 mole $l.^{-1}$ at 25°C. The solubility diagram for the system thallous nitrite–water has been reported.[323] A eutectic is formed[323] at -7°C. containing 1 mole-% of thallium nitrite. The ultra-violet spectrum[324] of thallous nitrite shows a weak band at 464 mμ and a strong one at 355 mμ; the latter is caused by absorption of undissociated $TlNO_2$. Portions of the phase diagrams for the systems thallium nitrite with sodium nitrite and water, thallium nitrite with potassium nitrite and water and thallium nitrite with barium nitrite and water have been reported.[325] The solubility of thallium nitrite is notably increased by adding potassium nitrite[325] and with barium nitrite the double salt $2Ba(NO_2)_2,TlNO_2$ crystallizes out[289, 325] on isothermal evaporation of stoicheiometric solutions. The crystal structure of this double salt is rhombic, of space group D_{2h}^{11} (*Pbcm*) and sides *a* 13·480 A., *b* 17·940 A. and *c* 4·958 A., containing 4 stoicheiometric units. The thermal diagram of the fused system[325] thallium nitrite–thallium nitrate (Fig. 29) excludes the possibility of complex formation between these compounds but shows that thallium nitrite and nitrate form an uninterrupted series of mixed crystals.

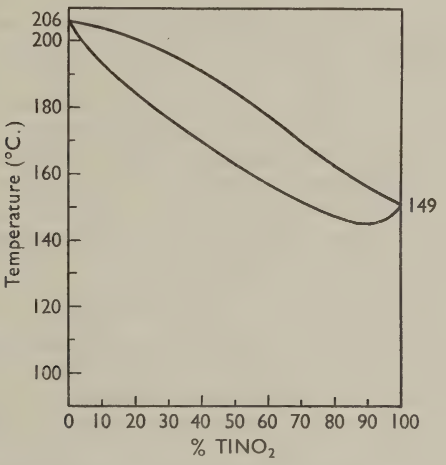

FIG. 29.—Thermal diagram for the system thallous nitrate–thallous nitrite: initial and final solidification temperatures

Pure *lead nitrite* has not been prepared in the solid state. Solutions of lead nitrite are obtained[327] by shaking lead bromide with silver nitrite when solutions up to 0·3 M. may be formed, but only freshly prepared solutions are free from nitrate, the nitrite changing to the nitrate and a basic salt. This decomposition is[327] catalysed by the photo-decomposition of silver bromide. Attempts[327] to form the nitrite by reducing lead nitrate with metallic lead in aqueous solution in a sealed tube at 25°C. failed, mixtures of the basic nitrate and nitrite being formed, with evolution of nitric oxide. At 100°C. in acetic acid the reduction and decomposition were enhanced.[327] A series of mixed salts containing lead ion, the potassium ion and the nitrite ion with and without potassium nitrate has been reported[328]; these salts have the formulæ $K_2Pb(NO_2)_2(NO_3)_2,H_2O$ with varying nitrite–nitrate compositions, $K_2Pb(NO_2)_3(NO_3),H_2O$, $K_3Pb_2(NO_2)_7,H_2O$ with slightly varying potassium nitrate compositions and $K_2Pb(NO_2)_4,H_2O$. Some *X*-ray investigation of these compounds has been undertaken.[328]

Chromium nitrite. The nitropentamminechromium (III), $[Cr(NH_3)_5NO_2]^{2+}$, cation has been prepared[204] by adding 30 g. of sodium nitrite to a slightly warmed solution of aquopentamminechromium (III) perchlorate (10 g.) in 100 ml. water containing a little acetic acid. After cooling and filtering the resulting nitropentamminechromium (III) nitrite can be washed with alcohol and ether and dried; it can be purified by reprecipitation from weak acetic acid solution with sodium nitrite. If sodium perchlorate is used for this last step nitropentamminechromium (III) perchlorate is formed.[204] The compound is stated[204] to exist in the nitritito form. Its ultra-violet spectrum shows two absorption maxima[204] at 20730 and 28060 cm.$^{-1}$

Iron nitrite. Iron forms the triple nitrite $K_2Pb[Fe(NO_2)_6]$ (Mellor, VIII, 501) which has a magnetic moment[291, 329] of 0·9 B.M. and it has been suggested[330] that this indicates that the complex ion $[Fe(NO_2)_6]^{3-}$ is 'covalent'.

Uncomplexed *cobalt nitrite* has not been reported. The pyridinates of cobalt (II) nitrite have been prepared[331, 332]; the compound $[Co(C_5H_5N)_6](NO_2)_2$ is formed when a solution of cobalt (II) nitrate hexahydrate (30 g.) and pyridine (25 g.) in 100 ml. of water is treated with a solution of sodium nitrite (15 g.) dissolved in the minimum quantity of water. The reaction must be carried out in a hydrogen atmosphere at 0°C. The initial product is the tripyridinate $Co(C_5H_5N)_3(NO_2)_2$; recrystallization from pyridine in which the tripyridinate is very soluble gives the hexapyridinate. This red compound when kept over concentrated sulphuric acid in a vacuum desiccator yields[332] first the rose-red tripyridinate and then the deep-red dipyridinate, $Co(C_5H_5N)_2.(NO_2)_2$. Water hydrolyses these pyridinates, and air oxidizes them to the nitrates.[331] The alternate action on the hexapyridinate of dry ammonia and standing over strong sulphuric acid in vacuo has resulted[333] in the formation of $[Co(NH_3)_6](NO_2)_2$ and $Co(NH_3)_4.(NO_2)_2$ as rose-red and ochre compounds respectively. The compound $2Co(NO_2)_2,3N_2H_4$[315] is a dull-red explosive compound. There is evidence[334] that nitropentamminecobalt (III), $[Co(NH_3)_5NO_2]^{2+}$, ions can be formed by the equilibrium:

$$Co(NH_3)_6{}^{3+} + NO_2{}^{-} \rightleftharpoons Co(NH_3)_5NO_2{}^{2+} + NH_3$$

in aqueous solution, and that this equilibrium is catalysed by activated carbon. The nitropentamminecobalt (III) salts can be prepared in two forms, the red and the yellow; the red form is far less stable and corresponds to the nitrito-form, while the yellow form corresponds to an equilibrium mixture of the nitrito- and more stable nitropentamminecobalt (III) ion.[335] The kinetics and equilibrium of the isomerization between the nitrito and nitro forms have been studied,[335, 336] but the second investigation quoted has been criticized[335] because the possibility of the reaction proceeding to an equilibrium rather than to completion was not considered. The activation energies for the change nitrito- to nitro and for the reverse reaction have been estimated[335] as 27·0 kcal. mole^{-1} and 25·2 kcal. mole^{-1} respectively and these results lead to a ΔH value of 1·8 kcal. mole^{-1}. The infra-red[337, 338] and ultra-violet[204] spectra of both these isomeric forms have been recorded. The heat of formation of the gaseous nitropentamminecobalt (III) ion has been estimated[339] as −257 kcal. mole^{-1} and the thermochemical radii calculated[339] as 2·30 Å. The kinetics of the formation of the nitritopentamminecobalt (III) ion from aquopentamminecobalt (III) ion and nitrous acid have been studied[340]; the rate of this reaction is 0·25 l.^{2} mole^{-2} min.$^{-1}$ at 25°C. By heating either *cis*- or *trans*-nitro-bis-ethylenediamineamminecobalt (III) nitrite, $[Coen_2NH_3(NO_2)](NO_2)_2$, *cis*-dinitro-bis-ethylenediaminecobalt (III) nitrite, $[Coen_2(NO_2)_2]NO_2$ and ammonia are formed,[341] the *trans* isomer being more reactive. The preparation of *cis*-nitroaquotetramminecobalt (III) nitrate has been described[342, 343] and its ultra-violet spectrum and rate of isomerization to the *trans*- form have been investigated.[343] The rate of isomerization is given as 5×10^{-4} min.$^{-1}$ at 30°C. *cis*-Nitritoaquotetramminecobalt (III) nitrate has been prepared[343] by treating carbonatotetramminecobalt (III) nitrate (5 g.) and sodium nitrite (10 g.) in 100 ml. of water at 0°C. with 20 ml. of 10 N. nitric acid, keeping the temperature between 0° and 2°C. After five minutes the carmine-red precipitate of nitritoaquotetramminecobalt (III) nitrate can be filtered off and washed with 2 N. nitric acid, ethanol and ether. The product decomposes to the nitro-compound and must be stored in a refrigerated desiccator. The yield is reported as 48%. The ultra-violet spectrum of this compound has been reported.[343] The rate of conversion to *cis*-nitroaquotetramminecobalt (III) ion is[343] $2{\cdot}3 \times 10^{-2}$ min.$^{-1}$ at 30°C. The rate of formation of *cis*-nitroaquo-bis-ethylenediaminecobalt (III) ion, $[Coen_2H_2ONO_2]^{2+}$, from *cis*-chloronitro-bis-ethylenediaminecobalt (III) ion and water is[340] 7×10^{-3} l. mole^{-1} min.$^{-1}$ at 25°C. The rate of reaction of this ion (and of the *trans* isomer) with thiocyanate and azide ion[344] and with nitrite ion[340, 344] has been studied. The latter, with the *cis*- compound, leads to the formation of the *cis*-dinitro-bis-ethylenediaminecobalt (III) ion, $[Coen_2(NO_2)_2]^+$ with a rate constant of 8×10^{-3} l. mole^{-1} min.$^{-1}$ at 25°C. The *cis*-iosmer has also been formed by heating either *cis*- or *trans*-bis-ethylenediaminediamminecobalt (III) nitrite, $[Coen_2(NH_3)_2](NO_2)_3$, with an accompanying loss of two molecules of ammonia.[341] *cis*-Dinitrotetramminecobalt (III) nitrite, $[Co(NH_3)_4(NO_2)_2](NO_2)$, has been formed[345, 346] by heating nitropentamminecobalt (III) nitrite at 130–135°C. More extensive heating of this and the *trans*-isomer is reported to produce trinitrotriamminecobalt (III), $[Co(NH_3)_3(NO_2)_3]$. The structure of *cis*- and *trans*-dinitrotetramminecobalt (III) ion has been discussed[347] in the light of refractometric data and a Co–N bond length of 2·0 A. estimated in this ion and also in the trinitrotriamminecobalt (III) molecule, the tetranitrodiamminecobalt (III) anion and the hexanitrocobalt (III) anion. The free energy, heat and entropy of solution of *cis*- and *trans*-dinitrotetramminecobalt (III) sulphate have been determined[348, 349] for the mixed solvents ethanol–water and acetone–water as a function of solvent composition and dielectric constant at 298° Abs. The reaction of dichloro-bis-ethylenediaminecobalt (III) chloride with sodium nitrite is reported to be almost instantaneous; when cobalt (II) ions are present which act as a catalyst, dinitro-bis-ethylenediaminecobalt (III) salts are formed.[350] The mechanism of this reaction has been discussed.[350] The rate of conversion of the less stable *cis*- and *trans*-dinitrito-bis-ethylenediaminecobalt (III) to dinitro-bis-ethylenediaminecobalt (III) ions has been studied[351, 352] and is said to be faster than the corresponding isomerism of the mononitrocompounds. The preparation and ultra-violet spectrum of the nitronitrito-bis-ethylenediaminecobalt (III) ion have been described.[352] The ammonia ligands in the potassium, ammonium and thallium salts of the tetranitrodiamminecobalt (III) ion, $[Co(NH_3)_2(NO_2)_4]^-$ are reported[353, 354] to have the *trans* configuration. *X*-Ray analysis of the potassium and ammonium salts has shown that these are isometric, with an orthorhombic unit cell of space group D_2^1 (*P*222) containing 4 molecular units.[354] The structure of the salts of the hexanitrocobalt (III) ion, $[Co(NO_2)_6]^{3-}$ has been investigated[292]; they are cubic compounds of unit cell space group T_h^3 (*Fm*3). A Co–N bond length of 2·03 A.[292] is found for the potassium salt by assuming an N–O distance of 1·1 A. and an O–O distance in any NO_2 group of 2·1 A. The parameters for the ammonium salt are similar.[292] There is evidence[355] that the three ammonium ions in the ammonium salt are differently situated, two of them being surrounded by twelve oxygen atoms from twelve nitro groups, and the third ammonium ion being surrounded by twelve oxygen atoms from six nitro groups. Magnetic measurements[291, 356] on the hexanitrocobalt (III) ion have shown that it has a magnetic moment of 1·8–1·9 B.M. and hence[330] it is believed that the complex is of the 'covalent' type. The thermal decomposition of salts of the hexanitrocobalt (III) anion leads to the formation of large volumes of nitrogen, ammonia and water and this property has been made use of in a patent[357] using the potassium or rubidium salts for fire-proofing. The fact that with potassium, rubidium or cæsium salts this anion gives characteristic microcrystalline precipitates has been used in the qualitative detection of these metals.[358, 359] A variety of double salts may also be formed, thereby extending the versatility of the method.[358, 359]

Nickel nitrite is unknown in the solid state but occurs in a number of complex compounds. A variety of nickel pyridinates have been prepared[332]: the hexapyridinate, $[Ni(C_5H_5N)_6](NO_2)_2$ can be obtained as a deep blue compound by keeping the precipitate obtained by treating a solution of a nickel salt with sodium nitrite and pyridine at 0°C., in a dry atmosphere in the presence of pyridine. If this compound is kept in vacuo over concentrated sulphuric acid, pyridine is lost and the clear blue $Ni(C_5H_5N)_4.(NO_2)_2$ is formed.[332] The tetrapyridinate reacts with ammonia[360] to form the red tetramminenickel nitrite, $Ni(NH_3)_4.(NO_2)_2$ to which two further ammonia molecules are affixed, though with more difficulty, to give the red hexamminenickel nitrite, $[Ni(NH_3)_6](NO_2)_2$. The vapour pressure of ammonia above the last compound has been measured in the temperature range 15–115°C. At 200°C. in a current of dry air two molecules of ammonia are lost leaving a green decomposition product.[360] The preparation of $Cs_2Ba[Ni(NO_2)_6]$ has been described[288]; it is reported to be a coarse orange-brown powder. Thallous hexanitronickel (II) is obtained[289] by evaporating, in vacuo over concentrated sulphuric acid, the greenish yellow solution obtained by mixing a freshly prepared nickel nitrite solution (nickel salt plus sodium nitrite) with thallous nitrite. The compound is crystalline, has a meat-red colour and dissolves in water to give a green solution.[289] Magnetic measurements[291, 356] on the salts of the hexanitronickel (II) ion indicate a value of 2·9 to 3·1 B.M. for the magnetic moment, and hence it is deduced[330] that in this complex the bonding of the nitro groups has a much more 'ionic' character than in the corresponding iron and cobalt complexes. The preparation of the explosive hydrazine complex of nickel, $[Ni(N_2H_4)_2](NO_2)_2$, has been described.[316]

Ruthenium nitrite. The salt previously described as sodium ruthenium pentanitrite (Mellor, VIII, 513) is now believed[361] to be sodium hydroxytetranitronitrosylruthenium (IV) dihydrate, $Na_2[RuNO(NO_2)_4OH],2H_2O$.[361] This salt is soluble in water and a variety of organic solvents including ketones and alcohols. With 1 M. sulphuric acid at 65°C. it reacts[361] to form the salt of the trihydroxydinitronitrosylruthenium (IV) anion, $[RuNO(NO_2)_2(OH)_3]^{2-}$.

Rhodium nitrite. Trinitrotriamminerhodium (III) has been found as a by-product[362] in the preparation of potassium tetranitrodiamminerhodium (III) hemihydrate,[362] $K[Rh(NH_3)_2(NO_2)_4],0{\cdot}5H_2O$. The latter compound is obtained[362] by treating a boiling aqueous solution of diammonium sodium hexanitrorhodium (III), $(NH_4)_2Na[Rh(NO_2)_6]$, with concentrated ammonia solution (when a trace of trinitrotriamminerhodium (III), $[Rh(NH_3)_3(NO_2)_3]$ is precipitated as a by-product) and potassium chloride. The molar conductivity of potassium tetranitrodiamminerhodium (III)[362] at a 2000-fold dilution is 118·2 mhos. $cm.^{-1}$ The cæsium and tetrammineplatinum salts may be prepared[362] by precipitating a solution of the potassium salt with a solution of the appropriate cation. The preparation of the potassium and tetrammineplatinum pentanitroamminerhodium (III) salts, $K_2[RhNH_3(NO_2)_5]H_2O$ and $[Pt(NH_3)_4][RhNH_3(NO_2)_5]H_2O$, has been described.[363] Diammonium sodium hexanitrorhodium (III) is obtained[355] by reacting H_3RhCl_6 with sodium nitrite in the presence of ammonium chloride. The *X*-ray spectrum of this salt has been reported.[355]

Palladium nitrite. Dinitrodiamminepalladium (II), $[Pd(NH_3)_2(NO_2)_2]$, dinitrodiethylaminepalladium (II), $[Pd(C_2H_5NH_2)_2(NO_2)_2]$, and dinitrodi-*n*-propylaminepalladium (II), $[Pd(n\text{-}C_3H_7NH_2)_2(NO_2)_2]$ are prepared[364] by the action of sodium nitrite on the corresponding dichloro-, bromo-, iodo- or cyano-complexes. Both the *trans* and *cis* isomers have been prepared[364] and their melting and/or decomposition temperatures have been reported.[364] The series of salts $[PdA_2XNO_2]$, where $A = NH_3$ or $C_2H_5NH_2$ or $n\text{-}C_3H_7NH_2$ and $X = Cl^-$ or Br^- or I^- or CN^-, has been prepared.[364]

Iridium nitrite. Diammonium sodium hexanitroiridium (III), $(NH_4)_2Na[Ir(NO_2)_6]$, has been formed[355] in the same way as the corresponding rhodium complex, but the starting material was H_3IrCl_6. It is reported to be insoluble in ethanol and only slightly soluble in water.

Platinum nitrite. The equilibrium leading to the formation of hydroxynitrodiammineplatinum (II), $[Pt(NH_3)_2OHNO_2]$ and dinitrodiammineplatinum (II), $[Pt(NH_3)_2(NO_2)_2]$ from dihydroxydiammineplatinum (II) and sodium nitrite in aqueous solution has been measured.[365] Potassium dichloronitroammineplatinum (II), $K[PtNH_3.Cl_2.NO_2],H_2O$, has been prepared[366] by reacting potassium trichlorotriammineplatinum (II) with sodium nitrite. This compound formed a double salt, $K[PtNH_3Cl_2NO_2].[Pt(NH_3)_4]Cl_2$, with tetrammineplatinum (II) chloride, and if this double salt is ground in a mortar with an equivalent of potassium tetrachloroplatinum (II) and hot water, tetrammineplatinum (II)-tetrachloroplatinum (II) (removable by filtration) and pure potassium dichloronitroammineplatinum (II) monohydrate are formed.[366] Evaporation of the filtrate at 50°C. and then at room temperature, followed by grinding with ethanol, yields the pure potassium dichloronitrodiammineplatinum (II) monohydrate. This compound is hygroscopic and loses water at 110°C. It does not become anhydrous until it is heated to its melting point at 150°C. Treatment of this compound with pyridine results[366] in the formation of chloronitropyridinoammineplatinum(II), $[Pt(NH_3)(C_5H_5N)ClNO_2]$ which is a colourless solid, sparingly soluble in water. It has been stated[367] that in solution in the presence of potassium chloride the tetranitroplatinum (II) ion, $[Pt(NO_2)_4]^{2-}$, is converted into the dichlorodinitroplatinum (II) ion, $[Pt(NO_2)_2Cl_2]^{2-}$ and that this ion is more easily reduced polarographically than the parent tetranitroplatinum (II) ion.

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HYPONITROUS ACID AND HYPONITRITES

Hyponitrous acid is reported[1] to be formed in small traces when nitrous acid reacts with hydroxylamine (see p. 358).

Lithium hyponitrite has been prepared[2] by reducing a solution of lithium nitrate with magnesium amalgam until no nitrate or nitrite is detectable in the solution, filtering from the magnesium hydroxide and evaporating in a vacuum desiccator over concentrated sulphuric acid. After two weeks in the desiccator, impurity in the form of ammonium hydroxide is removed leaving lithium hyponitrite contaminated with lithium oxide. Repeated extraction with alcohol and precipitation with ether separates the lithium hyponitrite.

Sodium hyponitrite is said[3] to be formed as one of the products when sodium nitrite is reduced with carbon at elevated temperatures. Reduction of sodium nitrite with magnesium amalgam[2] or with sodium amalgam[4] has also been used in the preparation of sodium hyponitrite. The use of magnesium amalgam here is similar to its use in the preparation of lithium hyponitrite. A solution of sodium nitrite is reduced by slowly adding sodium amalgam and cooling, followed by separation of the aqueous layer and precipitation of the crude hyponitrite with alcohol; on dissolving in the minimum of water and allowing the solution to evaporate in a vacuum desiccator over sulphuric acid for 3–4 days needles of $Na_2N_2O_2,8H_2O$ result. The salt with 5 molecules of water of crystallization is obtained from a more dilute solution evaporated for a longer time under the same conditions. Sodium hyponitrite may also be prepared[5, 6, 7] in high yield by adding a solution of sodium ethoxide in absolute alcohol (6·62 g. of sodium dissolved in alcohol) to hydroxylamine hydrochloride (20 g.) in absolute alcohol. After cooling and filtering to remove the sodium chloride, sodium (15·4 g.) in alcohol is added, the solution

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cooled in a freezing mixture and the calculated amount of ethyl, amyl or propyl nitrite distilled in. Sodium hyponitrite is thus precipitated. The reactions are:

$$\mathrm{R{-}O{-}N{=}O + H_2NOH \rightarrow ROH + H_2N_2O_2}$$
$$\mathrm{H_2N_2O_2 + 2C_2H_5ONa \rightarrow Na_2N_2O_2 + 2C_2H_5OH}$$

where R = ethyl, propyl or amyl. Sodium hyponitrite decomposes on heating to give sodium oxide, sodium nitrite, sodium nitrate and nitrogen.[3, 4] This has been stated to occur at 260–265°C. *in vacuo*[4] and at 334–336°C. at atmospheric pressure.[3] Water and dilute acids partially decompose the hyponitrite to give nitrous oxide, nitric oxide and nitrogen,[4] whilst with concentrated sulphuric acid some nitric and nitrous acids are also formed.[4] Permanganate oxidizes sodium hyponitrite.[4]

The *hyponitrites* of *potassium*, $K_2N_2O_2$, *rubidium*, $Rb_2N_2O_2,2H_2O$, and *cæsium*, $Cs_2N_2O_2,4H_2O$, have been prepared[2] by reducing the corresponding nitrates with magnesium amalgam.

Silver hyponitrite may be prepared[5] by double decomposition between sodium hyponitrite and silver nitrate. It decomposes thermally as follows:

$$\mathrm{Ag_2N_2O_2 \rightarrow Ag_2O + N_2O}$$

and

$$\mathrm{3Ag_2N_2O_2 \rightarrow 2Ag_2O + 2AgNO_2 + 2N_2}$$

this decomposition being induced at 0°C. by dinitrogen tetroxide.[8] If silver hyponitrite is added slowly to an acid titanous chloride solution, nitrous oxide is evolved but no ammonia is formed.[9]

There is evidence that *beryllium hyponitrite* is formed as part of an insoluble product when beryllium nitrate solution is reduced with magnesium amalgam[10] below 5°C. but no pure salt was isolated.

Magnesium hyponitrite may be prepared, though not isolated in the pure state, by reducing magnesium nitrate with magnesium amalgam.[2]

Calcium hyponitrite, $CaN_2O_2,4H_2O$, *strontium hyponitrite*, $SrN_2O_2,5H_2O$, and *barium hyponitrite*, $BaN_2O_2,4H_2O$ have been prepared[2] by reducing their nitrates with magnesium amalgam. The thermal decomposition,

$$\mathrm{MN_2O_2 \rightarrow MO + N_2O}$$

and

$$\mathrm{3MN_2O_2 \rightarrow 2MO + M(NO_2)_2 + 2N_2}$$

(where M = Ca, Sr or Ba) has been investigated[11] and is reported[8] to be induced by dinitrogen tetroxide at 0°C.

The preparation of *zinc*, *cadmium* and basic *lead hyponitrites* by reducing aqueous solutions of the nitrates with magnesium amalgam has been described.[2]

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SECTION XXXIII

COMPOUNDS OF NITROGEN WITH THE HALOGENS

BY J. D. RICHARDS

NITROGEN FLUORIDES

Nitrogen Trifluoride

PREPARATION

When ammonia, diluted with nitrogen, is brought into contact with fluorine, up to 6 % of the ammonia is converted into nitrogen trifluoride.[1] Electrolysis of fused dry acid ammonium fluoride, NH_4HF_2, at 125° in a copper vessel (into which dips the cathode of an inverted copper cylinder attached to an insulated graphite anode) produces[1] hydrogen, nitrogen fluoride (NF_3), nitrous oxide, nitrogen, oxygen and ozone. 10 amp. at 7–9 v. was required and the resulting gases were led over granulated potassium fluoride and manganese dioxide (to remove ozone, hydrogen fluoride and water) and then cooled to $-75°$. The purified gas was passed successively through two glass vessels, both cooled with liquid air, the second being cooled further by passing a stream of chilled hydrogen through the bath. In the early experiments violent explosions due to ozone took place, but these were later avoided by using manganese dioxide to catalyse the decomposition of ozone to oxygen.[2] The removal of the difluoride NHF_2, and nitrous oxide, produced in the electrolytic preparation or by the action of ammonia and fluorine, is effected by passing the gases over soda-lime at 100°, then washing with warm acidified potassium iodide solution and finally fractionating.[3] The electrolysis of a mixture of ammonium fluoride and hydrogen fluoride gives nitrogen fluoride, NF_3, as the principal and primary product with yields of about 20%. The amounts of by-products, NH_2F, NHF_2 and nitrogen difluoride, NF_2, depend on the temperature and the ammonia concentration of the electrolyte. The NF_2 content is very small and it is obtained only from very acid solutions.[4] The best composition of the melt for the preparation of NF_3 is between NH_3,2HF and NH_3,3HF, and the temperature must be as low as possible as the fluorides decompose violently above 100°.[5] A more recent preparation is by electrolysis of molten ammonium fluoride, $(NH_4)_2F_2$, with a nickel anode, the anode gases being passed through concentrated potassium iodide solution and then *iso*pentane to a trap immersed in liquid nitrogen, followed by fractional distillation at 1 atm. pressure.[6]

PROPERTIES

Both liquid and gaseous nitrogen trifluoride are colourless.[15] The normal melting point[7] is reported to be $-208{\cdot}5°$ and the normal boiling point[8] is $-129{\cdot}0°$. The liquid density[16] at the m.p. is 1·92. The vapour tension curve[8] is given by

$$\log p = -\frac{662{\cdot}05}{T} + 1{\cdot}75 \log T - 0{\cdot}006607T + 4{\cdot}64615$$

where T = absolute temperature.

The latent heat[8] at 0° abs. is 3028 g.-cal./mol., and at the boiling point it is 2876 g.-cal./mol. The Trouton constant is 19·94 and the heat of formation[9] approximately 26 kcal. The triple point of NF_3, prepared by electrolysis of molten $(NH_4)_2F_2$, has been determined[6] as 66·37° abs. and the transition temperature, which occurs over a range of 0·05°, as 56·62° abs. The dielectric coefficient[10] is $0{\cdot}21 \times 10^{-18}$ and the molecular electric dipole moment[11, 12] of NF_3 obtained from the Stark effect of pure rotational spectra observed in the microwave region is $0{\cdot}234 \pm 0{\cdot}004$ Debye units for the ground vibrational state. From electron diffraction measurements[13] the NF_3 molecule is a symmetrical pyramid with $r_{N-F} = 1{\cdot}37$ A. and the F–N–F angle = 102·5°; the distance between adjacent fluorine atoms is 2·14 A. The small electric moment is due most probably to cancellation of the expected moment by a moment of opposite sign. This originates in electrical asymmetries resulting from imperfect balancing of the contributions of the unshared electrons of the nitrogen and fluorine atoms due in turn to the hybrid character of the nitrogen–fluorine bond orbitals.[14]

The nitrogen fluoride molecule is remarkably stable; the compound is unchanged by sparking and is almost insoluble in water.[15] If it is sparked with water vapour ignition occurs and hydrogen fluoride, nitric acid and nitrous acid result. Sparking with hydrogen gives nitrogen and hydrogen fluoride violently and a violent explosion also occurs by sparking with ammonia.[15] Traces of NF_3 are toxic; 1% in air causes blood poisoning and breathing such concentrations may be fatal in 30 minutes.[16] The use of nitrogen fluoride as a rocket fuel[17] has been studied and the maximum exhaust velocity with various reductants determined.

The physical constants of nitrogen trifluoride are summarized in Table I.

Table I.—Physical Constants of Nitrogen Trifluoride

Normal melting point	−208·5°
Normal boiling point	−129·0°
Liquid density at −208·5°	1·92
Latent heat at 0° abs.	3028 g.-cal./mol.
Latent heat at −129·0°	2876 g.-cal./mol.
Heat of formation	26 kcal. (approx.)
Triple point	66·37° abs.
Dielectric coefficient	$0{\cdot}21 \times 10^{-18}$
Molecular electric dipole	$0{\cdot}234 \pm 0{\cdot}004$ Debye units

Difluorodiazine

Another compound of nitrogen and fluorine is difluorodiazine, N_2F_2, prepared by the decomposition of fluorine azide.[18] From a study of the vapour the following configuration is concluded: F—N═N—F (*cis* and *trans*). The bond lengths for N—F and N═N are $1{\cdot}44 \pm 0{\cdot}04$ A. and $1{\cdot}25 \pm 0{\cdot}04$ A. respectively; with the N—N—F angle equal to 115 ± 5°.

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NITROGEN CHLORIDE

Preparation

Experiments by Noyes[1] showed that formation of nitrogen chloride, NCl_3, could not be detected when nitrogen mixed with chlorine is passed through a flaming arc, and that if any NCl_3 were formed it immediately decomposed as it left the hot zone. Noyes prepared nitrogen chloride from anhydrous ammonia and chlorine: $4NH_3 + 3Cl_2 \rightarrow 3NH_4Cl + NCl_3$, but found considerable decomposition of NCl_3 to nitrogen and chlorine. The ratios of the reacting gases can be varied within wide limits without appreciably affecting the ammonia: ammonium chloride ratio of 4:3.[2] Direct reaction between chlorine and ammonia diluted with an inert gas gives nitrogen chloride provided that the $NH_3:Cl_2$ ratio is less than 2:1; otherwise the irreversible reaction $NCl_3 + NH_3 \rightarrow 3HCl + N_2$ occurs. Dilution with air is preferred to prevent explosion, and mixing of the gases is carried out by injector spraying. To prevent clogging of the nozzle with ammonium chloride one of the gases can be slightly moistened.[3]

FROM AMMONIUM SALTS

The preparation of gaseous nitrogen chloride has been achieved by reaction in solution of chlorine with an ammonium compound. The solution is allowed to stand until the reaction is complete and the nitrogen chloride is removed by a current of air.[4, 5] After passing chlorine into a cooled (10°) stirred mixture of 240 g. of carbon tetrachloride, 60 g. of ammonium sulphate and 600 ml. of water for about 1 hr., a 12% solution of nitrogen chloride is obtained in the carbon tetrachloride layer after washing with 5% ammonium sulphate solution.[6] A continuous preparation has been suggested in which chlorine and diluent air are passed over a moist mixture of solid ammonium salts such that the flow rate of chlorine and air is adjusted to maintain the partial pressure of nitrogen chloride at 25–50 mm. with a total system pressure of about 1 atm. The carrier gas should contain substances capable of removing hydrogen chloride and other acids produced.[7] A mixture of nitrogen chloride and chlorine dioxide suitable for bleaching flour is obtained by blowing a stream of air and hydrogen chloride through a mixture of ammonium chloride and potassium chlorate in a molecular ratio of 1:6 respectively.[8, 9]

BY ELECTROLYSIS

Many authors confirm the preparation of nitrogen chloride by the electrolysis of aqueous ammonium chloride solution. It appears that a low concentration of ammonium ions in relation to chloride ions is required,[10] and an acidified solution of ammonium chloride in hydrochloric acid with at least 0·1 g.-mol. of free acid per g.-mol. of dissolved ammonium chloride is desirable.[11] The excess of chloride ions can also be achieved by adding either an alkali or alkaline earth chloride to restrict unwanted side reactions.[12] The removal of free acid during the electrolysis of ammonium chloride can be balanced by leaving sufficient nitrogen chloride in the solution to give an equivalent amount of free acid on decomposition.[13] Usually the nitrogen chloride is removed by a stream of oxygen, hydrogen or nitrogen with which is mixed chlorine gas in order to maintain the chloride ion and acid concentration.[10, 14, 15, 16] The conditions of electrolysis and the electrolytic cells are such that partial interaction of the nitrogen chloride with the electrolyte is sufficient to maintain constant acidity.

One cell is described with the anode in a porous tube connected to an absorption apparatus; the lower end of the tube has an angle piece which passes through the dividing wall separating the anode and cathode compartments.[17] Another way of causing this partial interaction is to place the jets which supply air to remove NCl_3 so as to cause downward movement of the electrolyte near the electrodes. The working conditions for graphite electrodes are 5–100 c.c. of electrolyte per sq. cm. of combined active surfaces of the electrodes and 100–2000 c.c. for platinum electrodes.

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The gas supply is about 30–300 l./min. per 100 litres of electrolyte.[18] A cell with approximately 100% current efficiency using a diaphragm and multiple cathodes has the following working conditions: one cathode is separated by the diaphragm from the anode and the other cathodes, and the separated cathode receives one-third of the total current. By neutralizing or blowing out with gas, the ammonia forming inside the diaphragm is kept at low concentration, and the electrolyte (NaCl–NH_4Cl solution) is continuously replenished.[19]

Under certain conditions electrolysis of ammonium chloride solution alone gives NCl_3 initially, but after the decomposition of all the ammonium ion only the perchlorate ion is present in a strongly acid solution.[20]

Properties

The heat of formation of nitrogen chloride in carbon tetrachloride has been computed as $-54{,}700$ g.-cal. per mol. from the reaction:

$$4HCl\ (gas) + NCl_3\ (in\ CCl_4) \rightarrow NH_4Cl\ (solid) + 3Cl_2\ (gas)$$

the heat of reaction being 41,800 ± 100 g.-cal. and the heats of solution of Cl_2 (gas) and HCl (gas) in CCl_4 being respectively 4539 and 3680 g.-cal per mol.[21]

The interaction between nitrogen chloride and nitric oxide has been studied and the products at various temperatures identified. Noyes found that at 0°C. the reaction between nitric oxide and nitrogen chloride in chloroform and carbon tetrachloride was chiefly the catalytic decomposition of nitrogen chloride; at -20°C. about a quarter of the nitrogen chloride was converted into chlorine and nitrous oxide and at -80° the main reaction is represented by the equation

$$NCl_3 + 2NO \rightarrow N_2O + NOCl + Cl_2$$

Nitrogen dichloride, NCl_2, was thought to be an intermediate but could not be isolated. At -150° the reaction takes place in four stages,[22] the overall reaction being $NCl_3 + 3NO \rightarrow 2NOCl + N_2O + Cl$, with NCl_2, N_2OCl_2 and N_2OCl as intermediates although they cannot be isolated. Further experiments by Noyes on the reaction between chlorine and nitric oxide in carbon tetrachloride at temperatures from -80° to -150° gave evidence favouring the hypothesis that the primary reaction[23] of nitrogen chloride in carbon tetrachloride with nitric oxide gives nitrosyl chloride, NOCl, and nitrogen dichloride, NCl_2, and that the latter then combines with nitric oxide to form N_2OCl_2. This then decomposes rapidly at -80°, but is sufficiently stable at -150° to yield a chlorine atom to a molecule of nitric oxide, although this combination to form nitrosyl chloride is slower than the decomposition of N_2OCl_2. In petroleum ether[24] between -130° and -140° no nitrosyl chloride is formed and the reaction $NCl_3 + NO \rightarrow N_2O + \frac{3}{2}Cl_2$ is believed to take place, the absence of NOCl being due to the formation of hydrogen chloride by the action of nitrogen chloride on petroleum ether which catalyses the reaction:

$$NOCl + NCl_3 \rightarrow N_2O + 2Cl_2$$

It has been found that dinitrogen tetroxide, N_2O_4, reacting with nitrogen chloride in chloroform at temperatures between 0° and 35°, gives nitrogen, oxygen, nitrous oxide, nitryl chloride and nitrosochloride. The formation of N_2O is due to loss of chlorine from N_2OCl_2 formed as an intermediate by the following reactions:

$$NCl_3 \rightarrow NCl_2^- + Cl^+$$
$$NOCl \rightarrow NO^+ + Cl^-$$
$$NCl_2^- + NO^+ \rightarrow N_2OCl_2$$
$$N_2OCl_2 \rightarrow N_2O + Cl_2$$

This reaction does not take place at -80° and is very slow even at -45°, although at temperatures at which reaction does take place (above -40°) it is violent if the solution of chloroform contains 25% or more of nitrogen chloride.[25]

DECOMPOSITION BY LIGHT

Earlier work on the electrolysis of ammonium chloride[26] showed the disturbing influence of light which caused the decomposition of some of the products. In the early 1930's Griffiths and Norrish[27, 28, 29] showed that nitrogen chloride undergoes photosensitized decomposition in the presence of excess of chlorine. The decomposition occurs by reaction chains of short length, the quantum efficiency falling to about 2 as the concentration of chlorine is increased. The quantum efficiency is primarily independent of the illuminated surface and vessel size, but the maturity of the vessel has an effect owing to a very thin film of ammonium chloride on the inner surface of the vessel causing chain rupture in the gas phase. The overall reaction is: $2NCl_3 \rightarrow N_2+3Cl_2$ which is of zero molecular order until nearly complete when a series of explosions occurs, the velocity of the reaction being proportional to the amount of light absorbed by the chlorine. Certain admixed gases, helium, argon, nitrogen and oxygen, in the NCl_3/Cl_2 mixture decrease the quantum efficiency to the limit of about 2. The proposed explanation is that the high energy nitrogen tetrachloride, NCl_4, which forms by triple collision and is associated with chain rupture, is stabilized by the added gas.

Experiments were made with light of wave-length 4360 A. and 3650 A., with the partial pressure of NCl_3 ranging from 0·146 to 2·48 mm. and that of chlorine from 22·3 to 706·6 mm. without admixed gas. It was found that for low pressures of chlorine (22–100 mm.) the quantum efficiency (γ) ranges between 17 and 5 and falls towards 3 as the pressure of chlorine is increased. An equation fitting the results so obtained for the quantum efficiency is $\gamma = 1/0{\cdot}0038P_{Cl_2} + 2{\cdot}5$ where P_{Cl_2} = partial pressure of chlorine. Green and yellow light do not produce decomposition. The decomposition of the mixture to which retarding gases have been added closely follows the equation: $\gamma = 1/0{\cdot}0038P_{Cl_2} + k_2P_{gas} + 2{\cdot}5$ where P_{gas} is the partial pressure of the added gas and k_2 is a constant for the gas, the values being 0·00093 for helium, 0·0016 for argon, 0·0017 for nitrogen, 0·0025 for oxygen and 0·0038 for carbon dioxide. The initiation of the decomposition is effected by chlorine atoms, although work on absorption spectra of aliphatic derivatives of chloroamines in solution suggests that the disruption of the N–Cl bond owing to absorption of ultra-violet light may also occur.[30]

DETONATION

The detonation of nitrogen chloride has been effected by supersonic waves. A very thin glass vessel containing NCl_3 was immersed in oil at about 2 cm. from an oscillating crystal (750,000 hertz) with a pressure amplitude of oscillation of about 2 atm. The detonation occurred in 9–10 seconds.[31] Detonation also occurs under impact of a 200 g. weight falling 1·2 cm. with a contact area of 0·25 sq. cm. Thermal impulse produces detonation. The impulse can be produced by discharging a condenser with a discharge time of 10^{-3} to 10^{-4} seconds through a thin platinum wire (2–5 μ diameter) which gives an instantaneous temperature pulse of a few thousand degrees. If the liquid is allowed to evaporate normally the detonation is less intense and may only result in a slow combustion. Increasing the pressure lowers the detonation temperature which can be reduced to approximately 170° at 100 atm.[32, 33] When liquid nitrogen chloride frozen in liquid air thaws *in vacuo* spontaneous explosion occurs[34] owing to the decomposition of the vapour. The vapour pressure at room temperature is about 150 mm. and the higher and lower limits for decomposition are 40 mm. and 10^{-3} mm. respectively at room temperature. Admixed air hinders the spontaneous reaction. Liquid nitrogen trichloride sealed in a glass tube and heated to 60° explodes after 13 seconds, although below 55° no explosion occurs, but liquid nitrogen chloride gradually evolves nitrogen and forms a solution in liquid chlorine, nitrogen chloride and liquid chlorine being mutually soluble.[34] Other publications[35, 36] confirm these findings. The detonation spectrum[37] of pure nitrogen trichloride (and of N_3Cl) by simple spark is continuous from the infra-red to the ultra-violet with a maximum between 5000 and 5500 A. The reactions $NCl_3 \rightarrow$

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$N + 3Cl$ and $N_3Cl \rightarrow 3N + Cl$ satisfy the explosion kinetics. The spectra are due to the recombination of the individual atoms. In the presence of water vapour bonds corresponding to NH, OH and ClO appear.

Uses

Nitrogen chloride has been used in the preparation of chlorine dioxide, ClO_2, by either of the following reactions:

(1) $NCl_3 + 3H_2O + 6NaClO_2 \rightarrow 6ClO_2\uparrow + 3NaCl + 3NaOH + NH_3\uparrow$

(2) $2NCl_3 + 6NaClO_2 \rightarrow 6ClO_2\uparrow + 6NaCl + N_2\uparrow$

The second reaction is preferable and gives yields between 64 and 93%, on the basis of chlorite consumption. In this method gaseous ammonia is passed through a bed of granulated sodium chlorite.[38] Theoretical considerations of the lowest heats of activation obtained by analysis of the possible mechanisms indicate that the hydrolysis of nitrogen chloride gives hypochlorous acid, HOCl, and ammonia, which is in accord with practical knowledge.[39] Other uses of nitrogen chloride include the refining of alloys, especially high quality aluminium alloys, by removing gases, oxides, carbides and nitrides.[40] The formation of nitrogen chloride in some water purification plants[41] gives rise to 'chlorinous odour' which is unpleasant both in smell and taste. Methods for its prevention and removal by activated carbon, aeration and dechlorination, with details of the plant and processes, have been described.[41]

Nitrogen chloride is used on the large scale in the bleaching and sterilizing of flour and other cereals. For this purpose it is usually prepared by electrolysing an acid solution of ammonium chloride at pH 4 between multiple cathodes and anodes of graphite wrapped in asbestos with a current rating of 20 amp. per anode at a potential difference of 3 to 4 v. An automatic current interrupter controls the plant so that the gas is supplied only when required. Another mode of preparation for this purpose is by feeding calcium hypochlorite, $Ca(OCl)_2$, into acid solutions of ammonium ions. The evolved gases are removed by air currents. Reducing the partial pressure of the nitrogen chloride up to a certain point improves the bleaching, and it is found that multiple bleaching gives better results than an equivalent amount added at one time. Bleaching efficiency depends on agitator loading and on the duration of treatment, temperature, the moisture content of the flour and velocity of reaction. Bleaching efficiency decreases with extent of treatment and the removal of pigment below 0·65 p.p.m. is not obtained by the usual treatment. Temperature is inversely related to bleaching efficiency which indicates that adsorption limits the action and more bleaching occurs for a constant rate at low temperatures (7–50°). At higher temperatures some reaction occurs with the flour constituents. Increased moisture content causes a decrease in bleaching efficiency. Unbleached flour is unaffected by mixing with treated flour.[42–50] A sterilizing and bleaching solution is prepared by the action of nitrogen chloride and air on an aqueous solution of ammonia or ammonium chloride, the exit gases being passed into a solution of ammonia of specific gravity 0·91.[51]

Nitrogen chloride is used as a chlorination agent in organic chemistry and in the preparation of chloroamines. It forms addition compounds with unsaturated compounds, e.g. hydrocarbons, ketones, acids, and *cyclo*hexene. With Grignard reagents primary amines are the main product with lesser amounts of secondary and tertiary amines and nitrogen.

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NITROGEN BROMIDE

The deep red oil alleged to be nitrogen tribromide, NBr_3, prepared by dropping potassium bromide on to nitrogen trichloride in water is probably the compound obtained by Schmeisser[1] having the formula $NBr_3,6NH_3$. This was prepared by mixing bromine and excess of ammonia at 1–2 mm. pressure in a trap at 20° to form ammonium chloride and a vapour which is condensed by cooling in an adjoining U-tube at $-75°$. The same compound was prepared[2] by glow discharge on a mixture

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of bromine and ammonia, but a better method of formation is to mix the gases at 100° and cool to −95° after precipitating ammonium bromide. The dark red oil explodes suddenly at −67° giving nitrogen, ammonium bromide and ammonia in proportions consistent with the formula $NBr_3,6NH_3$. By adding solid bromine[3] to a vigorously stirred mixture of liquid and solid ammonia, the heat of reaction being utilized by the fusion of solid ammonia so that the temperature remains at −78°, a bromine derivative of ammonia is obtained besides ammonium bromide and nitrogen. A pale reddish yellow colour is seen in the liquid ammonia solution at low concentrations at −50°, while at higher concentrations at −78° it is red, these colour changes being controllable by altering the conditions. A dark red-violet compound remains with the ammonium bromide after evaporation at −78°. Experiments on the decomposition of this compound show it to be rapid at −50° and slow at −70°, the rate-determining step following first order kinetics. Extraction from the liquid ammonia solution at −78° by diethyl ether partly removes bromine–nitrogen compounds, but another ethereal solution containing NH_2Br can be obtained after the removal of ammonia by means of cadmium chloride or copper sulphate. The dark red-violet compound is most probably that prepared by Schmeisser, $NBr_3,6NH_3$. This compound is best obtained by treating a solution of bromine in ethyl chloride with excess of ammonia at −70°. From the observations on the two coloured liquid ammonia solutions cited above, there seems to be an equilibrium of the nature: $x\mathrm{NH_2Br} + y\mathrm{NH_3} \rightleftharpoons$ red-violet compound, and if this is $NBr_3,6NH_3$ the equation is:

$$3\mathrm{NH_2Br} + 4\mathrm{NH_3} \rightleftharpoons \mathrm{NBr_3,6NH_3}$$

Another similar[4] dark red-violet compound has been formed by reaction between ammonia and BrNCO and ethyl chloride. The formula is presumed to be $BrNH_2$ or an ammoniate of this compound. Attempts to prepare[2] the compound NBr_3, by a glow discharge on a mixture of bromine and nitrogen did not result in combination of the elements.

From a curve plotting the known heat of formation of some nitrides of the elements against their atomic numbers, the heat of formation of nitrogen bromide ($\frac{1}{2}\mathrm{N_2} + \frac{3}{2}\mathrm{Br_2}$ liq. $= \mathrm{NBr_3}$) is predicted to be −80·3 kcal.[5] The wave number for the diatomic molecule NBr has been calculated.[6]

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NITROGEN IODIDE

Preparation

Raschig prepared a nitrogen iodide, NH_3,NI_3, (see also Mellor, II Suppl. 1, 1, 851) by adding 10–15 ml. of 10 N.-ammonia solution to 3–5 ml. of N-potassium iodide, filtering off the nitrogen iodide, washing for 30 seconds with cold water, dissolving in 20 ml. of 5N-hydrochloric acid and finally filtering. A third of the product decomposed to nitrogen and iodine on washing with 500 ml. of water for 2 hours, the remainder liberating ammonia and leaving NI_3.[1] Nitrogen iodide, NI_3, is formed by the action of ammonia on the less stable alkali dibromoiodides. Taking the potassium salt as typical, the reaction is:

$$3\mathrm{KIBr_2} + 4\mathrm{NH_3} \rightarrow 3\mathrm{KBr} + 3\mathrm{NH_4Br} + \mathrm{NI_3}$$

the probable mechanism being: $3\mathrm{KIBr_2} \rightleftharpoons 3\mathrm{KBr} + 3\mathrm{IBr}$, $3\mathrm{IBr} + \mathrm{NH_3} \rightarrow 3\mathrm{HBr} + \mathrm{NI_3}$, $3\mathrm{HBr} + 3\mathrm{NH_3} \rightarrow 3\mathrm{NH_4Br}$. The more stable dibromoiodides having very low dissociation pressures form addition compounds with ammonia.[2] The decolorization in the reaction between dilute iodine and ammonia solutions at relatively low pH is not due to hydrolysis to form HIO or $N_2H_3I_3$. The reaction is reversible, and assuming the formation of NH_2I the net reaction is:

$$2NH_3 + I_2 \rightarrow NH_2I + NH_4^+ + I^-$$

The precipitation of $N_2H_3I_3(NH_3,NI_3)$ from the reaction and its solubility in excess of ammonia are represented by the equations[3]:

$$NH_2I + 2I_2 + 3NH_3 \rightarrow NH_3,NI_3 + 2NH_4^+ + 2I^-$$

and

$$NH_3,NI_3 + NH_3 \rightarrow 3NH_2I$$

The hydrolysis of NH_3,NI_3 had previously been investigated and it was found that the maximum stability occurred at pH 10 in either the presence or the absence of ammonia. The reaction between ammonia and iodine in carbon tetrachloride forms addition compounds of the type $x\text{NH}_3,y\text{I}$ together with a slight amount of reduction to hydrogen iodide for which the equations suggested are: $NH_3 + I_3 \rightarrow NH_2I + HI$, $NH_2I + NH_3 \rightarrow N_2H_4 + HI$ and $NH_2I + H_2O \rightarrow NH_2OH + HI$.[4]

Green crystals of nitrogen iodide,[5] NI_3, containing excess of nitrogen, are prepared from iodine and liquid ammonia at −78°C. in an apparatus which enables all the ammonium iodide to be removed. The excess of nitrogen is not all removed on washing with diethyl ether, but this causes decomposition to a red-brown unidentified solid having a nitrogen:iodine ratio of between 1·1 and 1·2.

Properties

From calorimetric measurements on the reaction with hydrogen iodide in dilute aqueous solutions at 19° the heat of formation of NH_3,NI_3 from its elements is calculated to be 35 kcal.[6]

On drying, NH_3,NI_3 loses some ammonia to form the explosive NHI_2, and in reaction with sodium hydroxide the decomposition of NH_3,NI_3 occurs according to the equations:

$$NH_3,NI_3 + 4NaOH \rightarrow NH_3 + 3NaI + 2H_2O + NaNO_2$$

and

$$NH_3,NI_3 + 3NaOH \rightarrow N_2 + 3NaI + 3H_2O$$

In reaction with sodium sulphite the representative equation is:

$$NH_3,NI_3 + 3Na_2SO_3 + 3H_2O \rightarrow 2NH_3 + 3HI + 3Na_2SO_4$$

With hydrogen chloride the reactions are[7]:

$$NI_3,NH_3 + 5HCl \rightarrow 3ICl + 2NH_4Cl \quad \text{and} \quad NI_3,NH_3 + HCl \rightarrow NI_3 + NH_4Cl$$

Reaction between nitrogen iodide, NI_3, and potassium amide in liquid ammonia at −78°, either by adding nitrogen iodide to excess of amide or the amide to excess of nitrogen iodide, produces a dark red-violet solution instantaneously, after which the colour fades and then disappears with simultaneous evolution of nitrogen. The experiments show two reaction steps, one instantaneous and the other slow, giving an overall reaction represented by the equation:

$$NI_3 + 3NH_2^- \rightarrow N_2 + 3I^- + 2NH_3$$

The reddish colour of the 'instantaneous' compound is due to an anion of nitrogen iodide formed by the reaction: $NI_3 + 3NH_2^- \rightleftharpoons 3NHI^- + 3NH_3$. The second step is therefore: $3NHI^- \rightarrow N_2 + 3I^- + NH_3$. A similar result occurs when sodium amide is used instead of the potassium salt, but a black insoluble compound (as yet not identified) besides nitrogen iodide appears when only a little sodium amide has been added, followed by the red-violet colour on further addition of sodium amide solution. This black compound appears with very dilute amide solutions and, although it has been obtained with dilute solutions of potassium amide, it occurs to a more noticeable extent with sodium amide owing to the relatively low solubility of this compound which is 0·004 g./100 g. NH_3 at 25°. With silver amide, black $AgNH_2,NI_3$ is formed but no red-violet colour is developed. The black $AgNH_2,NI_3$ is stable in ice water but decomposes in water at room temperature (and faster in light) to silver iodide, nitrogen, iodine, and ammonia; explosions occasionally occur if the compound is dry. It is concluded from these experiments, and others using different basic amides, that the formation of the ion NHI^- depends on the basic strength of the metal amide.[7]

Light of ordinary intensity has no effect on the decomposition of NH_3,NI_3 and decomposition occurs at temperatures as low as $-190°$.[8] If freshly precipitated nitrogen iodide, NH_3,NI_3, is freed from water by phosphorus pentoxide in a vacuum, it decomposes as soon as the crystals are dry. Detonation occurs at 0°, and at $-11°$ with a time lag; at lower temperatures there is slow decomposition. On isolating the system a slight rise of pressure occurs followed by an induction period of between 1 and 2·5 hr. and thereafter a steady rise of pressure at a constant initial rate falling off gradually and then becoming very slow until the pressure reaches 0·02 cm. Hg. The reaction is represented by the equation:

$$2NH_3,NI_3 \rightarrow N_2 + 2NH_3 + 3I_2$$

Ammonia at 4×10^{-3} cm. pressure stops the reaction and its removal restarts the reaction after a time lag. Water vapour at 17×10^{-3} cm. pressure retards the reaction, but its removal causes an immediate increase in reaction. Iodine vapour at $-13°$ has no effect on the rate,[9] although adsorbed iodine crystals are reported to be chain-breaking. The effect of ammonia is considered to show that deammoniation is the initial step followed by rapid decomposition of the NI_3 molecule. In the isolated system, nitrogen retards the reaction by preventing the escape of ammonia from the surface. If the pressure of the permanent gases remains above 2×10^{-3} cm. decomposition occurs within 24 hr. into iodine and permanent gases without detonation.[10, 11] Detonation by shock results from crystal fracture leaving clean surfaces free from adsorbed ammonia or water vapour. The activation energy of decomposition is $19 \pm 1{\cdot}3$ kcal. Particle size determination[12] by photomicrography and the rate of decomposition compared with the Polanyi–Wigner equation: rate $= N\nu e^{-E/RT}$, where N is the number of molecules per sq. cm. of surface and ν is the lattice vibration (10^{13}), gives $E = 17$ to 20 kcal., in good agreement with the determination from the temperature coefficient. It seems therefore that the reaction takes place on the surface without involving chain reactions. At higher pressures the formation of ammonium iodide is probably due to secondary reaction between iodine and ammonia. From probability considerations a bimolecular reaction would be sufficient, although the calculated activation energy gives a value nearer 4.[13]

In a series of experiments on the sensitiveness of solid high explosives to impact using oscillograph recording methods, the impact–rebound time of the detonation of NI_3,NH_3 was found to exceed the impact–explosion time, the difference being made greater by the addition of hard foreign substances such as quartz. Soft substances had no effect.[14] Electron bombardment does not produce explosion, although α-particles from polonium cause detonation after sufficient exposure, the more intense being the radiation and the drier the sample the less is the bombardment time required.[15–17] Neutron bombardment of pure nitrogen iodide causes no detonation, but explosion occurs owing to fission of the iodide, if it is mixed with black uranium oxide UO_2. If this oxide is initially mixed in the solution of iodine in potassium iodide used to prepare the nitrogen iodide, the detonation occurs in a much shorter time.[18, 19] Nitrogen iodide, NH_3,NI_3, is affected by strong light; detonation has been observed at $-8°$ and $-78°$. The light must be within the blue to red region, although the amounts of energy required vary with the wave-length. Ultra-violet and infra-red light are ineffective. The rate of photolysis is faster in air than in ammonia, as would be expected, and also increases with rise in temperature: *e.g.*: Quantum yield at 18° in air = 0·25; in ammonia = 0·08; Quantum yield at 24°

in air = 0·40; in ammonia = 0·15. The decomposition seems to be due mainly to a local instantaneous temperature rise following absorption of light energy, and to a smaller extent to a weak photochemical effect.[20–23]

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NITROSYL FLUORIDE

Nitrosyl fluoride, NOF, was prepared by Ruff, Menzel and Neumann[1] by the interaction of fluorine with excess of nitric oxide. A modification of this preparation is the vapour–liquid fluorination[2] of nitric oxide in a 'Fluorothene' vessel, in which the reaction proceeds smoothly to give a 90% yield. The boiling point is −59·9° and the melting point −132·5°.[1] The vapour pressure–temperature curve is given by:

$$\log \text{v.p.} = -(7234/4{\cdot}573T) + 1{\cdot}75 \log T - (0{\cdot}0742T/4{\cdot}573) + 9{\cdot}6840;$$

the liquid density is given by:

$$d = 1{\cdot}919 - 0{\cdot}00278T$$

The molecular volume is 37·0 c.c. at the boiling point and 25·9 c.c. at 0°.[1] Detection by the Stark effect of the dipole moment components along the least (μ_a) and the intermediate (μ_b) principal inertial axes in pure rotational transition of the line 0_0–1_{-1} and two components of the line 3_{-2}–3_{-1} gave the following results[3]: $\mu_a = 1{\cdot}70$; $\mu_b = 0{\cdot}62$D. which give the interatomic distances N–F and N–O as 1·52 A. and 1·13 A. respectively, and the angle ONF as 110°. For the components along the bonds calculated values are: $\mu_{NF} = 1{\cdot}75$ and $\mu_{NO} = -0{\cdot}17$D. Upper and lower limits for the force constants and thermodynamic properties of nitrosyl fluoride have been calculated.[4] The force constants have also been calculated from vibrational spectra[5] and the formulæ from these results agree with accepted structures. Infra-red spectroscopic measurements[7] show that the nitrosyl fluoride molecule is nearly a prolate symmetric top.

Nitrosyl fluoride reacts with sodium hydroxide giving nitric oxide, sodium fluoride, sodium nitrite and sodium nitrate, but it has no reaction with iodine or amorphous carbon.[1] Nitrososulphuryl fluoride, $NOSO_2F$, reacts as a mixture of nitrosyl fluoride and sulphur dioxide and it therefore gives some modified reactions of nitrosyl fluoride. Nitrosyl fluoride is not formed by the action of cold dilute nitric acid on fluorine gas, but nitrogen oxyfluoride, sometimes called fluorine

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nitrate, NO_3F (see Mellor, Vol. 2, Suppl. 1, 59) is formed[8]; it is a powerful oxidizing gas which explodes on heating. The analogous thio-nitrosyl fluoride, NSF, has been prepared and its properties have been investigated.[9] The use of nitrosyl fluoride as a rocket fuel has been investigated[10] and the maximum exhaust velocities with various reductants have been determined.

Boric anhydride, phosphorus pentabromide, germanium dioxide and stannic tetrafluoride or chloride yield respectively the nitrosofluoride complexes BF_3,NOF, PF_5,NOF, GeF_4,2NOF and SnF_4,2NOF.[11]

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NITROSYL CHLORIDE

Preparation

FROM AQUA REGIA

The concentrated aqueous solution of a mixture of hydrochloric and nitric acids known as 'aqua regia' evolves nitrosyl chloride, NOCl, and chlorine according to the scheme $HNO_3 + 3HCl \rightleftharpoons NOCl + Cl_2 + 2H_2O$. Aqua regia in sealed glass tubes at 0°C. and 21°C. is a system of three phases (2 liquids and 1 gas) which do not form at atmospheric temperature and pressure; the upper liquid layer is rich in water and the lower is mainly nitrosyl chloride and chlorine.[1] In a sealed tube at room temperature the two liquid layers form slowly, but more quickly at 100°C. The reaction $HNO_3 + 3HCl \rightarrow NOCl\,(g) + Cl_2\,(g) + 2H_2O\,(l)$ is exothermic if pure liquid nitric acid and gaseous hydrogen chloride are used, but the reaction is endothermic if concentrated aqueous acids are employed.[2] The difficulty in using this reaction to prepare nitrosyl chloride lies in the extraction, cooling and drying of the product. One method proposed is to pass a 50–80% solution of nitric acid cooled to below 10°C. in direct contact with the nitrosyl chloride containing the admixed vapours of nitric acid, hydrochloric acid and water.[3] Another procedure is to bring the mixed vapours into contact with concentrated sulphuric acid in the presence of nitric acid or nitrogen dioxide at 25°C. This forms nitrosylsulphuric acid which is then caused to react with a metallic chloride to form nitrosyl chloride.[4]

FROM DINITROGEN TETROXIDE AND METAL CHLORIDES

Alkali metal chlorides give nitrosyl chloride on treatment with moist dinitrogen tetroxide, N_2O_4, or nitric acid. At room temperature gaseous dinitrogen tetroxide passed over potassium chloride gives the reaction: $KCl + N_2O_4 \rightarrow KNO_3 + NOCl$.[5] The free energy and enthalpy change for the reaction with the tetroxide and the dioxide have been calculated[6] as follows. For the reaction

$$KCl\,(s) + N_2O_4\,(g) \rightarrow KNO_3\,(s) + NOCl\,(g)$$

$\Delta F_{298\cdot1} = -4496$ g.-cal., $\Delta H_{291\cdot1} = -3683$ g.-cal., and for the reaction

$$KCl\,(s) + 2NO_2\,(g) \rightarrow KNO_3\,(s) + NOCl\,(g)$$

$\Delta F_{298 \cdot 1} = -5623$ g.-cal., $\Delta H_{291 \cdot 1} = -16{,}691$ g.-cal. This reaction also occurs if nitrogen dioxide reacts with aqueous potassium chloride solutions, the hydrogen halide concentration of which is less than that corresponding to the hydrogen halide vapour pressure of 1 mm.[6] Potassium chloride solution at 20°C. passed down a tower packed with rings against a counterflow of air containing 6% of dinitrogen tetroxide produces air containing nitrosyl chloride at the top of the tower and potassium nitrate solution at the bottom.[7]

FROM NITRIC ACID AND METAL CHLORIDES

Nitrates, chlorine and nitrosyl chloride are simultaneously produced by heating metallic chlorides (KCl, NaCl, $CaCl_2$, NH_4Cl, $AsCl_3$, $AlCl_3$, BCl_3, $SnCl_4$) with nitric acid. The aqueous acid must contain more than 440 g. of nitric acid per litre so that the acid will be at least 7 N. after the reaction. The gaseous reaction products, chlorine and nitrosyl chloride, can be separated by dephlegmation and, after crystallizing out the nitrates, the mother liquor can be used to continue the process with more chloride.[8] The reaction:

$$3NaCl\ (cryst.) + 4HNO_3\ (g) \rightarrow 3NaNO_3\ (cryst.) + NOCl\ (g) + Cl_2\ (g) + 2H_2O\ (g)$$

and the analogous reaction with potassium chloride have been performed with an air stream containing nitric acid and water. Low concentrations of water (0·015 g./l.) and nitric acid (0·5 g./l.) with a linear flow velocity of 130 cm./min. at 130° give an S-shaped curve for the conversion–time graph showing an initial acceleration. This shape does not occur for concentrations of water above 0·194 g./l. and in all cases the rate decreases as the reaction progresses and is zero before all the chloride has been converted. Higher water concentrations increase the rate and it was found that a rise in temperature from 145° to 175° caused a decrease. Potassium chloride reacts faster than the sodium salt and the reaction is markedly faster with polycrystals than single crystals. It is supposed that the reaction begins at discrete centres catalysed by water at the surface, and that the water may also accelerate diffusion across the solid nitrate layer.[9] Reaction with potassium chloride occurs at 105°.[10] An apparatus for collecting the products of the disintegration of alkali chlorides by excess of nitric acid is described.[11, 12] One method of separating nitrosyl chloride from a gaseous mixture with chlorine is to pass the mixture over ferric chloride at 0°C. to form the addition compound which is then decomposed to ferric chloride and nitrosyl chloride by heating in a vacuum.[13] The separation of a liquid mixture can be effected by a continuous rectifying process.[14]

FROM NITRIC OXIDE AND HYDROGEN CHLORIDE

The preparation of nitrosyl chloride is achieved rapidly and in high yield by the reaction of gaseous nitric oxide, hydrogen chloride and an oxidizing agent such as oxygen, nitric acid or an oxide of nitrogen where the valency of nitrogen is greater than 3. The reaction may be represented by the following equations:

$$4NO + 4HCl + O_2 \rightarrow 4NOCl + 2H_2O$$
$$2NO + 3HCl + HNO_3 \rightarrow 3NOCl + 2H_2O$$
$$NO + 2HCl + NO_2 \rightarrow 2NOCl + H_2O$$
$$4NO + 6HCl + N_2O_5 \rightarrow 6NOCl + 3H_2O$$

The ratio of nitric oxide and oxidizing agent used is stoicheiometric. The temperature can be varied from 0° to 200°C., but about 75°C. is preferred. The hydrogen chloride should be in excess so that it can be condensed with the water present forming a concentrated aqueous solution which prevents the formation of undesirable by-products.[15]

FROM NITRIC OXIDE AND CHLORINE

The well-established preparation by direct combination of nitric oxide and chlorine, $2NO + Cl_2 \rightarrow 2NOCl$, is rapid and gives a product of good quality. The use of catalysts such as activated alumina at 40° to 50° followed by condensation and fractionation to remove excess of chlorine is a satisfactory refinement. The reaction $2NO + Cl_2 \rightarrow 2NOCl$ is trimolecular and has been considered unusual, but it has been explained with reference to the Wigner spin conversion rule that a bimolecular reaction is unlikely because the ground state of the NO molecule is a doublet and the interaction between two doublets produces a singlet state, so that a trimolecular reaction is more likely.[16] Bodenstein[17] found that abnormalities in the temperature coefficient in the reaction may be explained by the presence of dimeric nitric oxide.

FROM NITROSYLSULPHURIC ACID

By treating fuming nitric acid with sulphur dioxide for 6–8 hr. below 5° crystals of nitrosylsulphuric acid separate. These are then treated with concentrated sulphuric acid and the oxides of nitrogen are removed by a stream of dry air passed at 100° for 3 to 4 hr. On passing dry hydrogen chloride at 55° through the reaction mixture, a vapour is produced from which nitrosyl chloride can be condensed at $-45°$. The product contains hydrogen chloride, but this is removed by refluxing for 30 min. below $-5°$ and then distilling the nitrosyl chloride.[18] Earlier authors worked in diffuse light to avoid photochemical decomposition.[19] The reaction between nitrosylsulphuric acid and dry sodium chloride gives nitrosyl chloride which can be freed from chlorine by forming the complex with mercuric chloride, $HgCl_2,NOCl$, which yields pure nitrosyl chloride on warming.[20]

MISCELLANEOUS METHODS

Alkyl nitrites and silicon tetrachloride at 20° to 35° form nitrosyl chloride and orthosilicate esters; thionyl chloride and alkyl nitrites give nitrosyl chloride and dialkyl sulphites; while arsenic trichloride and ethylene nitrite also give nitrosyl chloride.[21] A mode of formation from an inorganic nitrite is by heating a dry mixture of sodium nitrite and aluminium chloride:

$$2AlCl_3 + 3NaNO_2 \rightarrow 3NaCl + Al_2O_3 + 3NOCl$$

The reaction of excess of sulphuryl chloride with silver nitrite and that between phosphoryl chloride and sodium nitrite also give nitrosyl chloride.[22]

Noyes[23, 24, 25] represents the reaction between nitrogen chloride and nitric oxide at $-150°$C. as: $2NCl_3 + 6NO \rightarrow 4NOCl + 2N_2O + Cl_2$, and at $-80°$ as:

$$NCl_3 + 2NO \rightarrow NOCl + N_2O + Cl_2$$

At $-20°$ still less nitrosyl chloride, but more chlorine is formed, probably owing to the reaction between nitrogen chloride and nitrosyl chloride to form nitric oxide and chlorine which increases with temperature. The reaction between benzoyl chloride or acetyl chloride and nitrosylsulphuric acid[26] gives nitrosyl chloride, which also results, together with diethylammonium nitrate, from the conversion of diethylammonium chloride in liquid dinitrogen tetroxide.[27] Sulphuryl chloride and nitrogen dioxide in a sealed tube at 180° produce nitrosyl chloride,[28] as does the reaction between tellurium dichloride and liquid dinitrogen tetroxide.[30] Liquid dinitrogen tetroxide reacts with thionyl chloride to yield nitrosyl chloride; the addition of liquid sulphur dioxide increases the yield and this fact is thought to support the view that the dinitrogen tetroxide is in the polarized condition represented by $NO^{\delta+}–NO_3^{\delta-}$.[29] The kinetics of the fast reaction in which nitrosyl chloride is formed from nitryl chloride and nitric acid have been studied by absorptiometric methods.[31] A temperature range of 1° to 71° and a pressure range of 0·2 mm. to 384 mm. were used in two systems of different surface:volume ratio. The reaction: $ClNO_2 + NO \rightarrow NO_2 + NOCl$ was found to be homogeneous and of first order with respect to each reactant. The second order rate constant is expressed by $k = 0{\cdot}83 \times 10^{12} e^{-6900/RT}$ c.c. mole^{-1} sec.$^{-1}$ A process for drying nitrosyl chloride gas involves passing the gas into direct contact with its liquid so that the liquid absorbs the moisture and the gas is withdrawn substantially dry.[32]

Physical Properties

VAPOUR DENSITY

Vapour density measurements[33] over the range $-61{\cdot}5°$ to $-5{\cdot}4°$ fit the equation:

$$\log \text{v.p. (mm. Hg.)} = -(1332/T)+7{\cdot}867$$

Later measurements were made by Burns and Dainton[34] on a sample purified by four distillations from the solid at $-78°$ to a receiver at $-110°$ with continuous pumping and believed to be 99·9 to 100% pure; these gave the values:

for solid NOCl $\log \text{v.p. (mm. Hg.)} = -(1660\pm 32/T)+9{\cdot}37\pm 0{\cdot}20$

for liquid NOCl $\log \text{v.p. (mm. Hg.)} = -(1347\pm 6/T)+7{\cdot}922\pm 0{\cdot}025$

Partington and Whynes[35] propose the equation

$$\log \text{v.p. (mm. Hg.)} = -(1320/T)+7{\cdot}802$$

for temperatures between 203° abs. and 258° abs. Burg and McKenzie[96] give the following equation for measurements between -48°C. and -6°C.:

$$\log \text{v.p. (mm. Hg.)} = -(1378{\cdot}82/T)+1{\cdot}75 \log T-0{\cdot}0036716T+4{\cdot}74582$$

THERMAL PROPERTIES

The triple point of nitrosyl chloride is $-61{\cdot}5°$ at 38·6 mm. pressure,[36] and the best value for the normal boiling point appears to be $-5{\cdot}8°$.[33] The melting point is reported as $-59{\cdot}6°\pm 0{\cdot}3$,[34] while other authors[33, 37] agree on $-61{\cdot}5°$, at which temperature nitrosyl chloride freezes to blood-red feathery crystals which at liquid air temperatures become lemon-yellow.[37] The vapour is orange red. The heat of vaporization was earlier determined as 6091 g.-cal./mole over the range $-61{\cdot}5°$ to $-5{\cdot}4°$, but a more recent determination gives the figure 6160 ± 27 g.-cal./mole, and the heat of sublimation and fusion as 7590 ± 150 and 1430 ± 180 g.-cal./mole respectively. The orthobaric density of liquid nitrosyl chloride measured recently over the range 20·5°C. to 73·0°C. lies between 1·273 at 20·5° and 1·147 at 73·0°.[38] The critical temperature is reported to be 167·5 ± 35°C., the critical pressure from vapour pressure data as 90 atm.[38] and the critical density as 0·47 g./c.c.[38] Many authors[22] have determined the heat of formation and the most acceptable value for the reaction $\frac{1}{2}N_2\text{ (g)}+\frac{1}{2}Cl_2\text{ (g)}+\frac{1}{2}O_2\text{ (g)} \rightarrow NOCl\text{ (g)}$ is $\Delta H_{298}=12{\cdot}57$ kcal./mole. The value of the molar entropy S°_{298} computed by Beeson and Yost[39] of 63·0 g.-cal. deg.$^{-1}$ mole^{-1} is generally the most acceptable. The same authors give the standard free energy of formation ΔF°_{298} for gaseous nitrosyl chloride as 15·86 kcal./mole. Many other workers give values in good agreement.[22, 42] The free energy of formation[40] of aqueous nitrosyl chloride at 25° determined from the reaction

$$NOCl\text{ (aq.)}+H_2O\text{ (l.)} \rightarrow HNO_2\text{ (aq.)}+HCl\text{ (aq.)}$$

is 16·015 kcal., and the hydrolysis constant of NOCl at 25°C. has been determined as $(9{\cdot}0\pm 0{\cdot}3)\times 10^2$. The heat capacity, C_p, of gaseous nitrosyl chloride calculated from spectrographic data[39] and entropy measurements[42] is 9·5 g.-cal. deg.$^{-1}$ at 25°C., and the latent heat of vaporization is 6068 and 6091 g.-cal./mole from 203° to 258° abs. and 211° to 267° abs. respectively.[35] The heat of vaporization at higher temperatures can be calculated from the equation $L=0{\cdot}000665T\ (v_g-v_c)\mathrm{d}p/\mathrm{d}T$ where L = B.Th.U./lb.; v_g = c.c. per g.-mole of gas; v_c = c.c. per g.-mole of liquid; p = atms.

VISCOSITY, STRUCTURE, DIELECTRIC CONSTANT ETC.

Viscosity measurements[41, 43] give values which, owing to decomposition, are in excess of the calculated values. These measurements enable the viscosity of mixtures of nitric oxide, chlorine and nitrosyl chloride to be calculated within 2%. Liquid nitrosyl chloride is diamagnetic and in a singlet state, and the magnetic susceptibility of the gas at 25° has been detected.[44] Electron diffraction measurements show the non-linear structure of the nitrosyl chloride molecule[45,46]; the Cl–N–O angle is 116°±2° and the interatomic distances of Cl–N, Cl–O, and N–O are 1·94±0·02 A., 2·64±0·02 A. and 1·14±0·04 A. respectively. Infra-red absorption spectrum measurements[47] confirm the structural measurements and give the entropy as $S^\circ_{298} = 62{\cdot}4 \pm 1$ g.-cal. deg.$^{-1}$ mole^{-1}. The values of the moments of inertia from these measurements are $I_A = 9{\cdot}05$, $I_B = 147{\cdot}7$ and $I_C = 156{\cdot}7 \times 10^{-40}$ c.g.s. units. The N–O bond distance observed is shorter than that expected owing probably to the resonance between the structures $Cl^-(N{\equiv}O)^+$ and Cl—N=O. Support for this theory is found in the high dielectric constant observed in carbon tetrachloride, 18·2 at 12°C., and in the fact that the observed dipole moment differs greatly from the calculated value.[48] The dielectric constant of liquid nitrosyl chloride is 19·7, 21·4 and 22·5 at −10°, −19·5° and −27° respectively.[49, 93] Determinations of bond order from vibrational spectra support the accepted structures.[50]

The specific conductivity of nitrosyl chloride is $2{\cdot}7 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ at −10°, which indicates that self-ionization in the liquid is small; even in solutions in liquid sulphur dioxide and dinitrogen tetroxide (which have high dielectric constants of 13·5 and 2·42 respectively) the dissociation is only slight.[51]

ABSORPTION SPECTRA

Experimental evidence relating to absorption spectra has been reviewed[52] and the absorption of light by nitrosyl chloride has been used to follow gas phase equilibria.[53] Kistiakowsky[54] showed that the quantum yield when gaseous nitrosyl chloride undergoes photochemical decomposition is about 2. This is in agreement with later work by Natanson[55] who gives an average quantum yield of 2·14 for pressures between 7·2 and 103 mm. This figure is unchanged in the presence of fifty-fold amounts of nitrogen or carbon dioxide. The activation mechanisms proposed by Kistiakowsky[54] are not generally accepted and the primary reaction is thought to be $NOCl + h\nu \rightarrow NO + Cl$.[55] The absorption spectrum below 530 mμ is continuous and photochemical decomposition takes place by primary dissociation in this region between 537 mμ and 618 mμ, rather than by collision with excited nitrosyl chloride molecules.[55, 56] The effect of an inert solvent on the efficiency of the primary process is illustrated by the quantum yield in solution of between 0·5 and 0·7.[57] The back reaction between nitric oxide and chlorine is eliminated by the introduction of oxygen and the low quantum yield agrees with the expected effect of solvent deactivation.

The physical constants of nitrosyl chloride are summarized in Table II.

Table II.—Physical Constants of Nitrosyl Chloride

Normal melting point	−59·6±0·3°
Normal boiling point	−5·8
Triple point	−61·5 at 38·6 mm.
Orthobaric density (20·5° to 73°)	1·273 to 1·147
Critical temperature	167·5°C.
Critical pressure	90 atm.
Critical density	0·47 g./c.c.
Heat of formation ΔH_{298}	12·57 kcal. mole^{-1}
Heat of vaporization	6160±27 g.-cal. mole^{-1}
Heat of sublimation	7590±150 g.-cal. mole^{-1}
Heat of fusion	1430±180 g.-cal. mole^{-1}
Molar entropy S°_{298}	63·0 g.-cal. deg.$^{-1}$ mole^{-1}
Standard free energy of formation of gas ΔF°_{298}	15·86 kcal. mole^{-1}
Dielectric constant at −10°	19·7
at −19·5°	21·4
at −27°	22·5
Specific conductivity at −10°	$2{\cdot}7 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$

Chemical Properties

THERMAL DECOMPOSITION

The equilibrium constant for the thermal decomposition of nitrosyl chloride at various temperatures to an equilibrium mixture according to the equation:

$$2NOCl \rightleftharpoons 2NO + Cl_2$$

has been determined by various workers. The data for the equilibrium constant are expressed by Dixon[58] by the equation

$$\log_{10} K_p \text{ (atm.)} = -(3860/T) + 3{\cdot}348 \log_{10} T - 0{\cdot}002457T - 1{\cdot}8275$$

and by Beeson and Yost[59] by the equation

$$\log_{10} K_p \text{ (cm. Hg.)} = -2{\cdot}808 - (3591{\cdot}0/T) + 4{\cdot}1457 \log_{10} T - 0{\cdot}0023406T + 0{\cdot}52915 \times 10^{-6}T^2 \pm 0{\cdot}02$$

From the latter equation the degree of dissociation of nitrosyl chloride has been computed to be 0·4% at 20°C. under its own vapour pressure, 3·2% at the critical point, 0·6% at 25°C. under 1 atm. and 6·9% at 125°C. under 1 atm.[38] The rate of decomposition at 300° in a static system is faster than would be expected[60] from other work.[61] This is reported to be due to the accelerating effect of chlorine on the initial rate because of the reaction: $NO + Cl_2 \rightarrow NOCl + Cl$ followed by:

$$Cl + NOCl \rightarrow NO + Cl_2$$

and this decomposition becomes more significant at higher temperatures than the bimolecular decomposition: $2NOCl \rightarrow 2NO + Cl_2$.[60] The decomposition is homogeneous with a bimolecular rate constant given by $4{\cdot}3 \times 10^{11}T^{1/2} e^{-24{,}000/RT}$ c.c. mole^{-1} sec.$^{-1}$ and it has been shown that 1 in 10 of the collisions between activated molecules results in reaction. The reverse reaction is trimolecular with a rate constant given by the equation[62] $3{\cdot}15 \times 10^{10}T^{1/2} e^{-6860/RT}$ c.c. mole^{-1} sec.$^{-1}$ This is in agreement with experiments on the formation of nitrosyl chloride between 273·2° and 463° in which the temperature quotient was found to be small.[63] The third-order reaction between nitric oxide and chlorine is discussed by Welinsky and Taylor[61] and the abnormalities in the temperature coefficient are explained by Bodenstein[17] on the basis of nitric oxide dimerization. The kinetics of the liquid phase reaction of nitric oxide and liquid chlorine or chlorine in carbon tetrachloride show a rapid reaction at −80°, the rate being appreciable at −150°, but much less at −180°[25] The rising energy of activation for the equation: $2NO + Cl_2 \rightarrow 2NOCl$ seems to be a function of the temperature.[61, 62] In the range 150° to 250° it is 6860 g.-cal. while the activation energy for the decomposition is found to be 24 kcal.[62] Experiments on the decomposition designed to decrease recombination gave results agreeing with theoretical calculations. The rate is unaffected by packing the vertical silica reaction tube with lumps of silica, thus indicating the probable absence of any catalytic effect of the walls. The temperature coefficient and energy of activation from these experiments were 1·025 and 6 kcal. respectively.[64] A study of the system Cl_2–NOCl by measuring partial and total vapour pressures in equilibrium with the liquid over the entire concentration range and at temperatures from −57·5° to −5° shows that the boiling point at 760 mm. varies smoothly from −35° to −5°. No evidence of compound formation at these temperatures was found.[65]

CATALYTIC ACTION

Small concentrations of nitrosyl chloride lower the ignition temperature of the hydrogen–oxygen reaction by over 200° and the sensitization is not affected by radiation from a mercury lamp. Nitrosyl chloride can act as an anticatalyst as well as a catalyst, the effective initial centres being chlorine atoms released by dissociation.[66] Experiments on the induction period and ignition limits of mixtures of oxygen and hydrogen in the proportions $2H_2:O_2$ at 180 mm. pressure and 360°

gave the following results for the addition of nitrosyl chloride: When the partial pressure of nitrosyl chloride is between 0·22 and 6 mm. the induction period is about 20 sec., but when 0·5 mm. of nitrosyl chloride is added to the reaction vessel first and the hydrogen–oxygen mixture after 30 sec., instantaneous ignition occurs. Other experiments introducing nitric oxide first and then the hydrogen–oxygen mixture also gave instantaneous ignition over a wide range of partial pressures of nitric oxide. Induction periods, or no ignition at all, occur when nitric oxide is introduced first and then nitrosyl chloride added with the hydrogen–oxygen mixture. It is concluded that sensitization by nitrosyl chloride is attributable to nitric oxide produced by decomposition and that nitrosyl chloride is chiefly a chain terminator.[67] Traces of nitrosyl chloride retard the photosynthesis of phosgene, $COCl_2$, from carbon monoxide and chlorine. Similar curves are obtained for inhibited and uninhibited reactions and the rate of the inhibited reaction at constant incident light from a carbon arc is given by

$$d[COCl_2]/dt = A[CO][Cl_2]^n/[NOCl](B[CO]+C)$$

where A, B and C are constants and n is about 1·85 for chlorine pressures up to 300 mm. but decreases at higher pressures. The chain mechanism suggested for the inhibited reaction[68] is:

(1) $Cl_2 + h\nu \rightarrow Cl + Cl$

(2) $CO + Cl \rightarrow COCl$

(2′) $COCl \rightarrow CO + Cl$

(3) $COCl + Cl_2 \rightarrow COCl_2 + Cl$

(5) $Cl + NOCl \rightarrow NO + Cl_2$

(6) $COCl + NOCl \rightarrow NO + CO + Cl_2$

The kinetics of the photochemical reaction in the presence of minute amounts of nitrosyl chloride have been determined at 25°, 40° and 55°; for the reaction

(*a*) $Cl + NOCl \rightarrow NO + Cl_2$

the rate $k_1 = 10^{10\cdot06}e^{-1\cdot06\ \text{kcal.}/RT}$ and for the reaction

(*b*) $COCl + NOCl \rightarrow Cl_2 + CO + NO$ (or $COCl_2 + NO$)

the rate $k_2 = 10^{10\cdot68}e^{-1\cdot14\ \text{kcal.}/RT}$. The potential energy diagram for reaction (*a*) assumed that the NO unit can be treated as an atom, that 20% of the binding is coulombic and that the problem can be treated as a 3*S* electron problem. The activation energy depends on the arbitrarily chosen fraction of the binding which is coulombic.[69] Nitrosyl chloride has been found to eliminate explosions in mixtures of hydrogen, chlorine and nitrogen trichloride.[70] The formation of nitrosyl chloride in the decomposition of chloropicrin has been used to follow the hydrogen–oxygen reaction sensitized by chloropicrin.[71]

OXIDATION TO CHLORINE

Nitrosyl chloride is decomposed by oxidation into a mixture of nitrogen dioxide and chlorine. This reaction is utilized in the formation of alkali metal nitrates from solid alkali metal chlorides. The mixture of gases is led over the solid chloride which is converted into the nitrate, some nitrosyl chloride being reformed at the same time and then oxidized. A circulatory system can therefore be used.[72, 73, 74] In another process nitrosyl chloride is passed into a saturated solution of sodium nitrate and sodium chloride at about 30° to 80°C. The nitric oxide formed with hydrochloric and nitric acids is withdrawn and, after neutralizing, sodium nitrate and chloride are crystallized.[75] The oxidation of nitrosyl chloride to nitrogen dioxide and chlorine represented by the equation: $NOCl + \frac{1}{2}O_2 \rightarrow NO_2 + \frac{1}{2}Cl_2$ and also its formation by the reaction: $3NaCl+4HNO_3 \rightarrow 3NaNO_3+Cl_2+NOCl+2H_2O$ have been studied as possible methods for the large scale production of chlorine.[76] The free-energy change for the former reaction is given by

$$-\Delta F = -5070+2{\cdot}75T\ln T-0{\cdot}0028T^2+0{\cdot}31\times10^{-6}T^3-11{\cdot}57T$$

which gives values at 100, 300, 500, 800, 1000° abs. of $-\Delta F = 4990, 4017, 3003, 1154, 230$ g.-cal. respectively. At higher temperatures nitrogen dioxide decomposes to nitric oxide and oxygen and the reactions:

$$(1) \qquad NO+\tfrac{1}{2}Cl_2 \rightarrow NOCl$$

and

$$(2) \qquad NO+\tfrac{1}{2}O_2 \rightarrow NO_2$$

become significant, although thermodynamically the reaction: $NO+\frac{1}{2}Cl_2 \rightarrow NOCl$ is repressed and decreased kinetically by increases of temperature. Thus the reaction $NO+\frac{1}{2}O_2 \rightarrow NO_2$ increases with rise in temperature, so that as the temperature rises the rates of reactions of (1) and (2) draw closer together, although reaction (1) lags behind reaction (2). Thus oxidation of nitrosyl chloride, produced from the reaction between sodium chloride and nitric acid, produces nitric oxide and this forms nitrogen dioxide rather than nitrosyl chloride and so oxidation of nitrosyl chloride, with air, in nitric acid occurs at temperatures below 300°. As nitrosyl chloride largely undergoes hydrolysis to hydrochloric and nitrous acids in concentrations of nitric acid below 60%, the nitric acid used in the production of chlorine must be above 70%.[76] Another author describes operation at 200° to 400° with 7 atm. pressure,[77] while others use 90% nitric acid in a closed circulating system.[78, 79] Excess of oxygen, lowering of temperature and removal of nitrogen dioxide by liquefaction or solution in water influence the reaction.[79] Details as to concentrations of nitric acid, temperature and pressure, and apparatus for the oxidation of nitrosyl chloride process are reported by many authors.[81, 82, 83, 84, 85] The separation and recovery of chlorine from the gaseous mixture after the oxidation reaction is effected by cooling and fractional distillation, or by absorbing nitrogen dioxide and nitrosyl chloride in concentrated nitric acid,[86] or by removing nitrogen dioxide in water or dilute nitric acid.[87] The separation of nitric oxide and chlorine obtained by thermal decomposition of nitrosyl chloride involves bringing the gaseous mixture into contact with a chemically inert solvent such as tetrachloroethane, $C_2H_2Cl_4$, in which one of the gases is more soluble.[88] The treatment of gas mixtures containing nitrosyl chloride with sulphur to form sulphur monochloride, S_2Cl_2, is used to remove NOCl. The sulphur monochloride is distilled at about atmospheric pressure with a small amount of ferric chloride, antimony trichloride or a mixture of them or iodine to produce monosulphur dichloride, SCl_2, which is then distilled to produce chlorine, the residue being used for treating further amounts of nitrosyl chloride. A variation of the use of sulphur monochloride is to heat the gaseous mixture with amounts of sulphur monochloride equivalent to the nitrosyl chloride content of the mixture. After cooling, the product is brought into contact with liquid sulphur monochloride containing 0·01% of antimony trichloride or ferric chloride, and the nitric oxide and much of the nitrosyl chloride are withdrawn, after which distillation at 10 atm. recovers the chlorine.[89] The use of catalysts such as silica gel[90] at temperatures not exceeding 600°, aluminium zeolite[91] at 200° to 300°, and manganese dioxide, ferric oxide or chromic oxide,[92] at 250° to 300°, moist carbonaceous material[93, 94] at atmospheric temperatures, manganous chloride and active charcoal,[92] in the decomposition of nitrosyl chloride has been reported. Nitrosyl chloride is decomposed to nitric oxide and hydrogen chloride by heating with admixed hydrogen to 400°. This mixture also reacts in contact with catalysts such as aluminium oxide, manganese dioxide, chromic oxide, silica and activated charcoal, or under the influence of suitable irradiation.[95]

IONIZING MEDIUM

Liquid nitrosyl chloride dissolves certain mononitrosyl salts to form strong electrolyte solutions. The ionization constant of mononitrosylferric tetrachloride, $NOFeCl_4$, in liquid nitrosyl chloride is 0·00373 at $-10°$. The solubility of $NOFeCl_4$ is 93 g. $FeCl_3$/100 g. NOCl at 0°, and it forms a solid solvate, $NOFeCl_4,NOCl$, with a dissociation pressure of 224 mm. at 0°.[96] Other examples of the solubility of mononitrosyl salts are found in nitrosylaluminium tetrachloride, $NOAlCl_4$, and nitrosylantimony hexachloride, $NOSbCl_6$. These also form strong electrolyte solutions in nitrosyl chloride and this high conductivity is due to the several resonance structures of the solvated nitrosyl ion NO^+. The dissociation pressure of the solid solvate, $NOAlCl_4,NOCl$, is reported to be 180 mm. by one author[96] and 240 mm. by another.[97] The solubility of nitrosylaluminium tetrachloride, $NOAlCl_4$, is 61·2 g. $AlCl_3$/100 g. NOCl at $-25°$, 68·2 at 0° and 93·0 at 18°.[96] Dinitrosylstannic hexachloride, $(NO)_2SnCl_6$, the corresponding titanium compound, $(NO)_2TiCl_6$, and nitrosylsulphuric acid are insoluble and non-conducting in liquid nitrosyl chloride as is potassium chloride. Dinitrosylpyrosulphuric acid, $(NO)_2S_2O_7$, gives a slight conductivity after 2 hr., which then slowly decreases. Sulphuric acid is inert. The formation of nitrosyl chloride in an acid–base type of neutralization is demonstrated by the reaction of nitrosyl salts and tetramethylammonium chloride, Me_4NCl. The electrolysis of nitrosylferric tetrachloride, $NOFeCl_4$, in nitrosyl chloride gives nitric oxide at the cathode and chlorine at the anode. The transfer of the nitrosyl ion, NO^+, is thought to be a solvo-chain mechanism due to the $NO^+:FeCl_4^-$ transference ratio of 7:1.[96] Nitrosyl salts in liquid sulphur dioxide react with iodides to liberate iodine and with azides to form nitrous oxide and nitrogen,[98, 99] the reactions being:

$$2NOX+2I^- \rightarrow 2NO+I_2+2X^-$$

and

$$NO^+ + N_3^- \rightarrow N_2O+N_2$$

Ionic reactions also occur in liquid dinitrogen tetroxide and the reaction between nitrosyl chloride and silver nitrate: $NOCl+AgNO_3\ (s) \rightarrow AgCl\ (s)+N_2O_4\ (l)$, is complete and comparable with the reaction between aqueous hydrochloric acid and insoluble hydroxides.[100] There are no compounds formed in the binary system $NOCl–N_2O_4$, but a simple eutectic occurs in the liquidus curve at $-74·8°$.[101]

COMPOUNDS WITH CHLORIDES

Much has been published on compound formation between nitrosyl chloride and various chlorides. The reactions between liquid nitrosyl chloride and dry metallic chlorides to form the complexes $SbCl_5,NOCl$, $SnCl_4,2NOCl$, $TiCl_4,2NOCl$, $PbCl_4,2NOCl$, $AlCl_3,NOCl$, $BiCl_3,NOCl$ and $FeCl_3,NOCl$ were reported by Rheinboldt and Wasserfuhr in 1927[102] and by Gall and Mengdehl in the same year.[103] The formation of $PtCl_2,2NOCl$ from platinum or platinum chloride ($PtCl_2$ or $PtCl_4$); of $BCl_3,NOCl$, which melts between 26° and 27° to two liquid layers one of which disappears at 65°, from boron trichloride; of red $PdCl_2,2NOCl$ from palladous chloride, or from palladous nitrate $Pd(NO_3)_2$—palladium metal giving a mixture of $PdCl_2,2NOCl$ and $PdCl_2,2NO$—and of $AuCl_3,NOCl$ from gold chloride, $AuCl_3$, or gold, in each case by reaction with nitrosyl chloride, has also been described.[37] The reaction of nitrosyl chloride and mercury gives mercurous chloride at $-40°$, but at $-20°$ oxidation occurs to mercuric chloride which then yields $HgCl_2,NOCl$. Silver nitrate and nitrosyl chloride react quantitatively at room temperature to form silver chloride and dinitrogen tetroxide, and lead nitrate reacts similarly, but barium, potassium and sodium nitrates show no reaction.[37] The formation, from nitrosyl chloride as a liquid at low temperatures or under pressure at 100°, of $CuCl,NOCl$ from copper, cuprous oxide or cuprous chloride, of $ZnCl_2,NOCl$ from zinc, of $MnCl_2,NOCl$ from manganous chloride, of $GaCl_3,NOCl$ from gallium or gallium chloride, $GaCl_3$, and of $InCl_3,NOCl$ from indium bromide, $InBr_3$, or indium chloride, $InCl_3$, has also been reported.[104] The reaction of thallous chloride, thallous oxide, thallous nitrate, or thallous nitrite with nitrosyl chloride at −20° produces thallium chloride, Tl_2Cl_3, but at 100° the latter compound reacts with nitrosyl chloride to form $TlCl_3,NOCl$. Similarly thallium first forms Tl_2Cl_3 at 100° and then $TlCl_3,NOCl$.[104] The reactions to form nitrosyl chloride addition compounds with acidic aqueous solutions of metallic chloride have also been described.[105] Magnetochemical investigations of some of these compounds[106] have shown that loose compounds occur between nitrosyl chloride and zinc chloride, aluminium chloride and mercuric chloride, while the formation of complexes, $[CuNO]Cl_2$ and $[MnNO]Cl_3$, with cuprous chloride and manganous chloride is indicated by their paramagnetism. Other compounds have been assigned the following formulæ:

$$[SbCl_6]^-(NO)^+;\ [SnCl_6]^{--}(NO)_2^{++};\ [PtCl_6]^{--}(NO)_2^{++}$$

Recent tracer study experiments in liquid nitrosyl chloride suggest the ionization of nitrosyl chloride to NO^+ and Cl^- ions,[107, 108] and this is the mechanism by which a complete exchange of chlorine occurs between labelled tetramethyl ammonium chloride[36] and solvent nitrosyl chloride. Other experiments[108, 109, 110] with the labelled compounds $FeCl_3,NOCl$, $SbCl_5,NOCl$, $AsCl_3$, CCl_4 and $POCl_3$ show the nature of the complexes. Rapid exchange occurred with the antimony and iron complexes owing to their existence as $NO^+(FeCl_4^-)$ and $NO^+(SbCl_6^-)$, and exchange was also complete between arsenious chloride and the solvent nitrosyl chloride involving either $AsCl_2^+$ or $AsCl_4^-$ ions. As carbon tetrachloride has no vacant orbitals for complexing there was no exchange,[109] but slow exchange resulted with phosphorus oxychloride, which is attributed to free chloride ions. From similar experiments[110] the ionic concentration and the ionic product $[NO^+][Cl^-]$ in nitrosyl chloride are reported as 10^{-8} g.-ion/l. and 10^{-6} g.-ion²/l.² respectively. Phase studies indicate the formation of $AsCl_3,2NOCl$.[110] The exchange of ^{36}Cl between adsorbed nitrosyl chloride[111] and zinc chloride, mercuric chloride and cadmium chloride is rapid and is followed by a slow heterogeneous exchange with excess of solvent. Unstable 1:1-nitrosonium salts are formed and the path for the heterogeneous change is the decomposition of the nitrosonium salt. In agreement with this, no exchange occurs between nitrosyl chloride and stable nitrosonium salts, sodium chloride or potassium chloride or chlorides not complexing with nitrosyl chloride. Silver chloride, which does not complex in the dark, shows only a slow heterogeneous exchange in light.[106, 109] Earlier experiments[112] on the action of anhydrous silver salts and nitrosyl chloride in a sealed tube at ordinary temperatures show (*a*) production of nitrosyl derivatives by double decomposition, e.g., N_2O_4 and nitrosyl perchlorate, $NOClO_4$, from silver nitrate and silver perchlorate respectively; (*b*) production of silver chloride and the liberation of the anion, e.g., silver thiocyanate and silver iodide, usually accompanied in the case of oxy-salts by a secondary reaction; and (*c*) complete oxidation and the reduction of nitrosyl chloride to nitrogen or nitric oxide. Investigation[113] into the binary system $NOCl$–$AlCl_3$ reveals two compounds, $NOCl,AlCl_3$ (congruent melting point 180°) and $2NOCl,AlCl_3$ (transformation point 17·5°) and a two-liquid layer region extending from about 84 to 99 mole-% $AlCl_3$. The temperature of the three-phase equilibrium between solid aluminium chloride and the two liquids is about 195·2°. The compound $NOCl,AlCl_3$ can be sublimed undecomposed in a high vacuum and its properties are intermediate between those of the pure heteropolar and molecular compounds. The bright yellow easily sublimed $NO(SbCl_6)$ formed from nitrosyl chloride and antimony pentachloride is also formed by the reaction of the acetyl complex $Ac[SbCl_6]$ (formed by the reaction between $SbCl_5$ and AcCl in liquid sulphur dioxide) with nitrosyl chloride according to the equation $Ac[SbCl_6] + NOCl \rightarrow NO[SbCl_6] + AcCl$. The conductivity of a 0·02 M. solution of nitrosyl chloride in liquid sulphur dioxide is $0{\cdot}6 \times 10^{-6}$ at −70° and $1{\cdot}5 \times 10^{-6}$ at 0°. Reaction between zinc and liquid mixtures of nitrosyl chloride and dinitrogen tetroxide containing up to 85% NOCl[115] forms

$Zn(NO_3)_2,2N_2O_4$ and $ZnCl_2,NOCl$, but above concentrations of 85% NOCl only the latter compound is produced. The rate of reaction at 0° over a concentration range of 10–40% NOCl is proportional to the square of the nitrosyl chloride concentration, but between 0% and 10% it is greater. The reaction represented by the equation: $Zn+2NOCl \rightarrow ZnCl_2+2NO$ is the rate-controlling step, except in low concentrations of nitrosyl chloride where the reaction between zinc and dinitrogen tetroxide is enhanced by the high dielectric constant of nitrosyl chloride. Pure zinc chloride is produced on heating $ZnCl_2,NOCl$ to 100°. If $Zn(NO_3)_2,2N_2O_4$ is treated with nitrosyl chloride at −10° for 1 hr., $ZnCl_2,NOCl$ is obtained as a white powder after evaporating off excess nitrosyl chloride at 20°. If the excess is removed at 0°, $ZnCl_2,N_2O_4,NOCl$ forms as a very pale yellow free-flowing powder which at 20° forms $ZnCl_2,NOCl$. There is evidence of this compound being in the dimeric form with the zinc in 4-co-ordinated form.

MISCELLANEOUS REACTIONS

The reaction of iodine and nitrosyl chloride gives nitric oxide and iodine chloride[116] and with nitrosoamine, $H_2N{\cdot}NO$, nitrosyl chloride reacts to form a little nitrogen trichloride.[117] Nitrosyl chloride in gaseous nitrogen reacts with solid sodamide[117] according to the postulated equation:

$$3NaNH_2+2NOCl \rightarrow 2NaCl+NaNO_2+2NH_3+N_2$$

The reactions of nitrosyl chloride with certain silicates[119] give the metallic chlorides. On the assumption of nitrosonium ion exchange, the reaction between nitrosyl chloride and sodium metasilicate is represented by the equation:

$$Na_2SiO_3+2NOCl \rightarrow (NO)_2SiO_3+2NaCl \rightarrow N_2O_3+SiO_2+2NaCl$$

With silver analcite, nitrosonium analcite and silver chloride are formed. There is no reaction with sodium or thallium chabazite but physical sorption probably occurs. The white nitrosylvanadium hexafluoride, $NOVF_6$, is obtained from vanadium pentoxide, bromine trifluoride, and excess of nitrosyl chloride on evaporation at 20°.[118, 120]

The corrosive action of nitrosyl chloride and its mixtures with chlorine in industrial processes has necessitated the use of resistant alloys. Nickel and alloys containing 45% or more of this metal with silicon or metals such as molybdenum, chromium, copper, or iron[121] are found to resist corrosion. Cast iron containing 15·75% of silicon or 15·3% of silicon with 3·8% of molybdenum is entirely resistant under the conditions of the reaction between nitric acid and sodium chloride[122] in the molecular ratio of 3:1 respectively at 100°. An iron alloy containing 2·39% of silicon and 31·95% of chromium has good resistance and the resistance to corrosion of certain proprietary alloys under various conditions and states of dryness has been reported.[122]

Carefully purified ozone and nitrosyl chloride show no reaction until small amounts of nitrogen pentoxide are added to the ozone, when a fast homogeneous reaction occurs with the stoicheiometry $NOCl+O_3 \rightarrow NO_2Cl+O_2$. The reaction is of one-half order with a large excess of ozone in the presence of nitrogen pentoxide, and one-half order rates have been found for both reactants.[123, 124] A logarithmic plot indicates one-half order dependence on nitrogen pentoxide and the reaction could be presented by the equations:

$$NO_2+O_3 \rightarrow NO_3+O_2$$

and

$$NOCl+NO_3 \xrightarrow{k_2} NO_2Cl+NO_2$$

The energy of activation of k_2 is about 6 kcal.[123] The oxidation of nitrosyl chloride by oxygen to nitryl chloride, NO_2Cl, is slow at room temperatures, but the rate increases rapidly with additions of dinitrogen tetroxide. Nitryl chloride (see also

p. 437) is also obtained by oxidation with nitrogen pentoxide, according to the equation: $N_2O_5 + NOCl \rightarrow N_2O_4 + NO_2Cl$.[125] The hydrolysis reaction between nitrosyl chloride (crystallized under vacuum) and potassium hydroxide in a sealed tube under reduced pressure gives nitric oxide.[126] From results of experiments in which the concentration and amount of potassium hydroxide were varied, the reaction $NOCl + KOH \rightarrow KCl + HNO_2$ was found to take place, after which the nitrous acid decomposes according to the equation $3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$. Emission of electrons has been observed when the liquid alloy of sodium and potassium, viz. NaK_2, comes into contact with various active gases. Among these nitrosyl chloride is exceptional in that emission still occurs of the order 10^{-13} to 10^{-12} amp. even on prolonged pumping out of the reaction chamber for several hours. Resulting curves of the energy distribution, current and pressure curves, and details of the work function of the alloy have been recorded from experimental data.[127]

Uses

Nitrosyl chloride is used for the treatment of flour[128] and in many organic reactions. Dithiocyanogen, $(SCN)_2$, may be prepared in a special apparatus by the reaction of nitrosyl chloride in a sealed ampoule with potassium thiocyanate in liquid sulphur dioxide at −30°, using a concentration of 1 g. KSCN in 25 c.c. SO_2. The dithiocyanogen is recovered by cooling to −50° and distilling the sulphur dioxide into a receiver cooled with liquid air; during this distillation the nitrosyl thiocyanate, ONSCN, which is the primary product, decomposes to $(SCN)_2$. The potassium chloride which is also formed is removed by filtration after dissolving the dithiocyanogen in liquid sulphur dioxide and then the sulphur dioxide is again distilled off.[129] Detergent, wetting and dispersing agents are prepared by reaction of nitrosyl chloride with olefine-containing mixtures of petroleum hydrocarbons,[130] and diesel fuel components are formed by reaction with mercaptans.[131] The action of nitrosyl chloride in concentrations of 0·03 to 0·35 mole-% on samples of furnace carbon black of pH 9·1 at 75°F. for 10 to 30 minutes gives a product of pH between 3·6 and 7·7.[132]

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NITROSYL BROMIDE

Much work has been reported on the mechanism of formation of nitrosyl bromide, NOBr. A series of papers by Bodenstein[1] in 1936 gave information regarding the equilibrium of nitrosyl bromide and showed that its formation from gaseous nitric oxide and bromine vapour was trimolecular at all temperatures and concentration ratios. This confirmed the work of other authors[2] who gave the heat of reaction for the equation: $2NO\ (g) + Br_2\ (g) \rightarrow 2NOBr\ (g)$ as

$$\varDelta H^\circ = -8780 - 13{\cdot}41T + 0{\cdot}0186T^2 - 11{\cdot}6 \times 10^{-6}T^3$$

and the free energy of formation as

$$\varDelta F^\circ = -8780 + 30{\cdot}88T \log_{10} T - 51{\cdot}26T - 0{\cdot}0186T^2 + 5{\cdot}8 \times 10^{-6}T^3$$

At 25° the free energy of formation of the gas from its elements is 19,260 g.-cal. The virtual entropy of gaseous nitrosyl chloride at 25° and 1 atm. is $65{\cdot}2 \pm 0{\cdot}3$ g.-cal./deg. Results of studies[3] of the gas phase equilibrium in the system NO–Br_2–Cl_2–$NOBr$–$NOCl$–$BrCl$ over the range 372° to 492°K. have been used in the determination of the thermodynamic constants of bromine chloride (see Mellor, Suppl 2, Pt. 1, 476). The trimolecular formation of nitrosyl bromide from bromine and nitric oxide is explained by reference to the Wigner spin conservation rule.[4] Most molecules have a singlet or triplet ground state, but nitrosyl bromide is a doublet and this makes a bimolecular reaction unlikely since the multiplicity of the potential energy surface cannot change during a reaction. Since interaction between two doublets produces a singlet state, the reaction $2NO + Br_2 \rightarrow 2NOBr$ is most likely to be trimolecular. The structure of nitrosyl bromide is non-linear,[5] the interatomic distances N–Br, Br–O, N–O being respectively $2{\cdot}14 \pm 0{\cdot}02$ A., $2{\cdot}85 \pm 0{\cdot}02$ A. and $1{\cdot}14 \pm 0{\cdot}04$ A.[5, 6] The bond order has been calculated for the oxyhalides of nitrogen using an equation obtained from vibrational spectra.[7] The dielectric constant in carbon tetrachloride at 15·2° is 13·4 and the high dipole moment (1·87D. from experimental work by Ketelaar,[6] who prepared pure nitrosyl bromide) suggests resonance between the homopolar form Br—N=O and the ionic structure $Br^-(N{\equiv}O)^+$.

The rate of hydrolysis of nitrosyl bromide according to the equation

$$NOBr + H_2O \rightarrow HNO_2 + H^+ + Br^-$$

is 8×10^6 at 0°. Nitrosyl bromide can be used as a nitrosating agent in buffer solutions, thus replacing nitrogen trioxide N_2O_3.[9] It can act as a brominating reagent for α- and β-amino-acids[10, 11] and it also forms addition products with *iso*butylene.[12] Nitrosyl compounds liberate iodine from iodides in liquid sulphur dioxide,[15] the reaction with nitrosyl bromide being $2NOBr + 2I^- \rightarrow 2NO + I_2 + 2Br^-$. With azides in liquid sulphur dioxide, nitrosyl bromide forms nitrous oxide and nitrogen.[15]

Nitrosyl tribromide, $NOBr_3$, is first formed as a red oil when nitric acid and hydrogen bromide are mixed.[13] This compound is also shown in the phase diagram of the system NO–NOBr, giving −40° as the melting point of nitrosyl tribromide and its density at 20° as 2·637.[14]

The formation of nitrosyl iodide, NOI, has not yet been achieved and it is thought to be incapable of existence.[16, 17]

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NITRYL FLUORIDE

Preparation

The reaction between nitrogen dioxide (in excess) and fluorine gives nitryl fluoride, NO_2F.[1] This reaction by vapour–liquid fluorination in a 'Fluorothene' vessel proceeds very smoothly to give a 90% yield of nitryl fluoride.[2] The rate of reaction between nitrogen dioxide and fluorine has been measured at 27·7°, 50·4° and 70·2°, light absorbed by the nitrogen dioxide being used to follow the reaction.[3] In low concentrations of the reactants the high rate was lowered to a convenient value and was found to be of first order for each reactant with no dependence on nitryl fluoride. The mechanism proposed is: $NO_2+F_2 \xrightarrow{k_1} NO_2F+F$ (slow) and $NO_2+F+M \xrightarrow{k_2} NO_2F+M$ (fast) where M represents a molecule of any one of the species present. From the rate constant $k = Ae^{-E/RT}$; $A = 1{\cdot}6 \times 10^{12}$ c.c. mole^{-1} sec.$^{-1}$ and $E = 10{\cdot}5$ kcal. Nitryl fluoride is also obtained by the condensation of dry nitrogen pentoxide on dry sodium fluoride in a closed system[4] in a vessel alternately warmed and cooled to liquid nitrogen temperatures, so as to remove the oxygen produced by the decomposition of nitrogen pentoxide. Nuclear magnetic resonance measurements on this product exhibit two large separations precluding the idea that splitting caused by the ^{14}N nucleus could be transferred through an intermediate oxygen atom. Nitryl fluoride is obtained by the reaction of sodium nitrite and fluorine in almost quantitative yield,[5] the equations for the reactions being:

$$2NaNO_2+F_2 \rightarrow 2NaF+2NO_2$$

and

$$2NO_2+F_2 \rightarrow 2NO_2F^{8}$$

A 5% yield of nitryl fluoride results from passing a stream of nitryl chloride over silver fluoride in a platinum tube at 240°.[6] It is also formed by heating nitryl borotetrafluoride, NO_2BF_4, with sodium chloride at 240° in a platinum tube.[6]

Properties

The structure[7] of nitryl fluoride is most probably $O_2N{-}F$ and not $O{-}N{-}O{-}F$. Analysis of infra-red absorption spectra on a sample of nitryl fluoride prepared from fluorine and sodium nitrite shows evidence of a planar C_{2v} molecule with the angle ONO = 145–155° and the interatomic distances, calculated from moments of inertia, N–O and N–F equal to 1·22 A. and 1·5 A., respectively. This evidence does not support a zig-zag or pyramidal structure. The physical constants of nitryl fluoride are summarized in Table III.[8]

Table III.—Physical Constants of Nitryl Fluoride

Melting point	−166°
Boiling point	−72·5°
Density at 65° above the m.p.	1·571 g. cm.$^{-3}$
Surface tension at −104·5°	27·6 dyne cm.$^{-1}$
Viscosity at 65° above the m.p.	0·00572
,, at the b.p.	0·00460
Critical temperature	76·3°
Vapour pressure at 65° above the m.p.	113·8
Heat of hydrolysis	31 kcal.
Heat of formation	26 kcal.

Nitryl fluoride is completely absorbed by sodium hydroxide to form sodium fluoride and sodium nitrate and it reacts with carbon and iodine.[1] Reactions[8] with metals fall into three groups, viz.,

(*a*) Those forming an oxide and a fluoride, i.e., sodium, potassium, silver, zinc, cadmium, aluminium, titanium, zirconium, thorium, tin, lead, manganese, iron and nickel. The equations for the reactions are:

$$M+2NO_2F \rightarrow MF_2+2NO_2$$
$$M+NO_2 \rightarrow MO+NO$$
$$NO_2+NO \rightarrow N_2O_3$$

where M is the metal.

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(*b*) Those forming oxyfluorides, i.e., chromium, molybdenum, tungsten and uranium, the reaction being $M+2NO_2F \rightarrow MO_2F_2+2NO$. At higher temperatures the oxyfluorides decompose to form the oxide and fluoride.

(*c*) Those metals which are unreactive below 300°, i.e., beryllium, magnesium, calcium and gold.

White solid compounds result from reactions[8] with most non-metals but not bromine and tellurium. Some examples of these compounds are represented by the following formulæ: $(NO_2)_2SiF_6$, $(NO_2)BF_4$, $(NO_2)_2GeF_6$, $(NO_2)AsF_6$, $(NO_2)SbF_6$, $(NO_2)SeF_5$, $(NO_2)IF_6$. The reactions take place in two stages, the first forming the fluoride; e.g., the equations for the boron reaction are: $B+3NO_2F \rightarrow BF_3+3NO_2$ and $BF_3+NO_2F \rightarrow (NO_2)BF_4$. Reaction with sulphur trioxide gives nitronium-fluorosulphonate, $(NO_2)SO_3F$. The substance formed by bubbling nitryl fluoride through bromine trifluoride probably contains nitronium bromine tetrafluoride, NO_2BrF_4. These nitronium salts evolve nitryl fluoride when heated with sodium fluoride, and on hydrolysis form nitric acid and the fluoro-acid. Tellurium reacts spontaneously at room temperature with the evolution of much heat to give a yellow liquid containing two fractions one of which may be tellurium tetrafluoride. The yellow colour is due to nitrogen dioxide. Vanadium pentoxide when gently warmed with nitryl fluoride reacts in stages; the mixture changes from dark-red to yellow, then to white, forming a vapour which freezes to a white solid. The primary products are vanadium oxytrifluoride, VOF_3, and vanadium pentafluoride which react with nitryl fluoride to give $(NO_2)VOF$ and $(NO_2)VF_6$, nitryl vanadium oxyfluoride and nitryl vanadium hexafluoride respectively. Nitryl fluoride is soluble in concentrated sulphuric acid and selenic acid giving a solution of concentration of about 2 moles NO_2F/mole of solvent. In phosphoric acid the solubility of nitryl fluoride is about 1·7 mole NO_2F/mole of solvent. In concentrations of up to 1 mole-% of NO_2F in sulphuric acid it reacts according to the equations:

$$\text{(i)} \qquad NO_2F+H_2SO_4 \rightarrow NO_2^+ +HF+HSO_4^-$$

and

$$\text{(ii)} \qquad HF+2H_2SO_4 \rightleftharpoons H_3O^+ +HSO_3F+HSO_4^-$$

and from 1 to 9·6 mole-% NO_2F (the point of maximum conductivity) the reaction $NO_2^+ +HSO_4^- \rightleftharpoons NO_2HSO_4$ continues after reaction (i) above. At 22 mole-% NO_2F the maximum viscosity is reached owing to the formation of nitrylsulphuric acid, NO_2HSO_4, counterbalanced by hydrogen fluoride, and at approximately 47 mole-% minimum conductivity occurs when all the sulphuric acid has been used up. The conductivity then increases up to a concentration of 68 mole-% of nitryl fluoride when a solid, identified as nitryl fluorosulphuric acid, NO_2SO_3F, separates. Nitryl fluoride, together with other compounds, has been investigated as a rocket fuel.[9]

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NITRYL CHLORIDE

Preparation

Nitryl chloride is obtained by the reaction of phosphorus pentachloride with nitric acid.[1] Schumacher and Sprenger[2, 3] prepared nitryl chloride by oxidizing nitrosyl chloride with ozone, the nitrosyl chloride being obtained by the combination of nitric oxide and dry chlorine and freed from any residual nitric oxide. The product of the nitrosyl chloride–ozone reaction, after cooling in liquid air, gives a colourless solid mass. Other preparations are by the action of nitrogen pentoxide on phosphorus chloride[4] and by that between nitric acid dehydrated with oleum and chlorosulphonic acid, $ClHSO_3$.[5, 6] By adding 1·4 mole of chlorosulphonic acid dropwise over 2 hr. to 1·4 mole of anhydrous nitric acid at −0·5° 1·1 moles of nitryl chloride are produced,[5] and this reaction can be used to provide a continuous stream of nitryl chloride.[7] According to another prescription,[8] 145·5 g. of distilled chlorosulphonic acid is added slowly to 200 g. of a mixture of 600 g. of 93·9% nitric acid and 813 g. of 104·5% oleum between 0° and 5° with constant agitation, giving 82–85 g. of nitryl chloride (about 80 to 83% yield) of 97 to 98% purity when the product is distilled at −70°. The use of nitric acid, undistilled chlorosulphonic acid or mixed nitrating acids more than 15 days old gives a lower yield and/or a less pure product. Mixtures of chlorine and dinitrogen tetroxide, N_2O_4, and nitrosyl chloride and oxygen on standing at room temperature develop spectra[9] observed in nitryl chloride. Chlorine obtained from sodium chloride and nitric acid usually contains 2–3% of nitryl chloride.[10]

Properties

Nitryl chloride is a white crystalline solid melting at −145° to a heavy colourless liquid boiling at −15·9° under 1 atm. pressure to give a colourless gas of density 2·81 at 100°. The density of the liquid at −80° is 1·5 g. $cm.^{-3}$ and at that temperature the viscosity is 0·00616 poise and the vapour pressure 16·1 mm.[2, 11] The viscosity at temperatures from −20° to −10° has also been measured in a series of experiments to ascertain the rate of molecular motion of the anhydrous halogen compounds by the Bachinskii formula.[12] The hydrolysis of nitryl chloride, corresponding to the equation: $NO_2Cl + H_2O \rightarrow HNO_2 + HOCl$, indicates that the molecule may be ONOCl, i.e., nitrosyl hypochlorite.[7] Experiments using azides, which are sensitive to nitrosyl groups, $(NO.X + N_3^- \rightarrow N_2 + N_2O + X^-)$ show no products of the hypochlorite ion ClO^-. Using tetramethylammonium azide the equation is:

$$2NO_2Cl + Me_4NN_3 \rightarrow Me_4NNO_3 + N_2 + N_2O + Cl_2$$

giving tetramethylammonium nitrate, nitrogen, nitrous oxide and chlorine as the products. This result is attributed to a primary decomposition to dinitrogen tetroxide and chlorine, after which the dinitrogen tetroxide reacts with the azide. Thus the structure of nitryl chloride is really that of a chloride of nitric acid.[7, 13] Results of spectrum measurements also confirm that the nitryl group $[NO_2]$ is present and that the molecule is planar and of the C_{2v} pattern.

Nitryl chloride decomposes at about 120° and this thermal decomposition has been studied by Sprenger and Schumacher whose findings[2, 15, 16] indicate a primary monomolecular reaction independent of pressure, according to the equation $NO_2Cl \rightarrow NO_2 + Cl$, followed by a secondary reaction indicated by the equation: $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$. Contaminating gases, viz., nitrogen dioxide, chlorine, nitrogen, oxygen, hydrogen and carbon monoxide, quicken the reaction, the effect of nitrogen dioxide being the greatest. Stoicheiometric amounts of nitrogen and chlorine act as unchanged nitryl chloride. The energy of dissociation of nitryl chloride given by the equation $NO_2Cl \rightarrow NO_2 + Cl$ has been calculated to be 32 kcal.[9, 17] The reaction between nitryl chloride and liquid ammonia at −75° is violent, yielding ammonium chloride, ammonium nitrite, hydrazine and monochloroamine, NH_4Cl, NH_4NO_2, H_4N_2, $ClNH_2$ respectively, but producing no

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nitrates. In the gas phase the same products are formed but with less violence. With stannic chloride, no reaction occurs but with stannic bromide bromine is evolved. An endothermic reaction occurs with phosphorus trichloride but none with boron trifluoride. Sulphur trioxide produces a violent reaction to give a voluminous precipitate. No reactions occur with silicon tetrachloride, tungsten dioxide, molybdenum trioxide, MoO_3, iodine pentoxide, sulphur dioxide or with the metals copper, magnesium, iron, aluminium and tin. Metallic bismuth, zinc and mercury give the chlorides.[5] The kinetics of the fast reaction between nitryl chloride and nitric oxide, studied by absorptiometric methods[20] with greatly differing surface to volume ratio, over a temperature range between 1° and 71°, with the pressure of the reactants ranging between 0·1 mm. and 18 mm. (total pressures between the range 0·2 and 384 mm.), show the quantitative reaction, represented by the equation:

$$ClNO_2 + NO \rightarrow NO_2 + ClNO$$

to be homogeneous and of first order with respect to each reactant, with a second order rate of $0{\cdot}83 \times 10^{12} e^{-6900/RT}$ c.c. mole^{-1} sec.$^{-1}$ Nitryl chloride reacts with many unsaturated organic compounds: e.g., ethylene in an inert solvent at room temperature gives 2-chloroethyl nitrite and 1-chloro-2-nitroethane, and in general the addition of nitryl chloride to ethylenes and acetylenes results in a good yield of the corresponding 1-chloro-2-nitro compound.[7] It has been shown that in polar solvents chlorination rather than nitration occurs, which may be due to free chlorine produced by traces of moisture according to the reaction:

$$3NO_2Cl + H_2O \rightarrow Cl_2 + NOCl + 2HNO_3$$

The presence of nitrosyl chloride in reactive solutions has been spectroscopically detected, but nonreactive solutions are colourless.[18]

The existence of nitryl bromide, NO_2Br, is doubtful, its preparation[19] apparently not having been confirmed.

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SECTION XXXIV

THE SPECTROSCOPY OF NITROGEN AND CERTAIN OF ITS COMPOUNDS

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THE SPECTRUM OF ATOMIC NITROGEN

BY A. THORNE

Introduction

The spectrum of atomic nitrogen was not thoroughly analysed until the years 1925–1935, in spite of the common occurrence of nitrogen. The spectrum is complex, and many of the strongest lines occur in the far ultra-violet region. Moreover, in many forms of light source in which nitrogen is present, the band spectrum of N_2 is the most prominent feature, particularly in the visible and near ultra-violet regions. The spectrum is of great interest in astrophysics: various nitrogen lines appear in the spectra of the aurora and the twilight glow, as well as in the spectra of many stars and nebulae.

The neutral nitrogen atom has the ground state configuration $1s^2\ 2s^2\ 2p^3\ {}^4S$; there are therefore three valence electrons, giving rise to a complex spectrum. General descriptions of such spectra are to be found in the textbooks, e.g.,[1, 2, 3, 4, 5] of which two[1, 2] refer specifically to the N I spectrum and give energy level diagrams. N II is carbon-like, with two valence electrons, and the successive states of ionization then give alternately one- and two-electron spectra. These are all, however, complicated by the number of terms in which an electron from one of the inner shells is excited.

Moore's Multiplet Tables[7, 8] list a very large number of multiplets of N I and N II in the infra-red, visible, and ultra-violet regions, together with a finding list arranged by wave-length. Wave-lengths may also be found in the Massachusetts Institute of Technology Wave-length Tables,[10] giving arc and spark lines of all elements between 10,000 A. and 2000 A., together with a list of all the 'raies ultimes'. Energy levels determined from measured wave-lengths were tabulated in 1932 by Bacher and Goudsmit[9] for N I, II, III, IV, and V. Much more comprehensive tables were published in 1948 by Moore,[6] giving energy levels for all the spectra from N I to N VII.

In 1938 Shenstone[11] gave a summary of the work done in analysing the arc and spark spectra of all elements, incorporating tables showing how thoroughly each spectrum had been investigated. Meggers[12] brought the information up to date in 1946. The classification ranges from *A* for a very well analysed spectrum to *E* for a scarcely known one, and in both papers the designations for the various nitrogen spectra are *A* for N II and N III, *B* for N I, IV, and V, and *E* for N VI. Hartree[146] presented in a similar way, also in 1946, a summary of the calculations of wave functions and energy levels that had then been carried out for all elements.

Many lines of the spectra N I to N V in the vacuum ultra-violet region are readily excited in sparks or condensed discharges in which small quantities of nitrogen are present, and such lines have been suggested as standards for this region of the spectrum.[13–21] Wave-lengths have been accurately measured for this purpose in the range 2000 A. to 100 A.[16–20]

Excitation

The spectrum of atomic nitrogen has been observed in various forms of arc, spark, and discharge tube. In early experiments, arrangements of electric and magnetic fields were used to distinguish between the N I and N II lines and to measure the lifetimes of the excited states.[22–27] N I lines were also studied in high current arcs run in air[28, 29, 76] and in low voltage arcs run in N_2[75] and in mixtures of N_2 with other gases.[30–34, 49] The excitation of nitrogen spectra in different forms of glow discharge was also described in early experiments[35, 36, 46, 47] and the conditions necessary for excitation of the different spectra were discussed.[37, 38, 45, 46, 48] The intensities of spectral lines excited by various positive ions, including alpha particles, have also been investigated.[39–41] In condensed discharges the changes in the spectrum with the strength of discharge have been described.[42–44, 98] The occurrence of lines from ions up to N IV, together with a strong continuum, has been studied in long sparks in air.[58–60]

The sources used to excite the spectra for systematic investigations include discharges in mixtures of helium and nitrogen, condensed or uncondensed,[75, 77–80, 98–100] pulsed electrodeless discharges,[61, 83] and various forms of spark and vacuum spark.[90, 93, 97, 103, 104, 106]

In recent years there has been much interest in the spectra produced by shock waves and high current arcs and by pinched discharges in gases at low pressures. When air or nitrogen is present, lines of the various states of ionization of nitrogen appear, and these have been used in some cases to estimate the conditions of temperature, pressure, etc., in the discharge. A few references to such work are given here,[50–56, 207] but for adequate information on this rapidly developing subject reference must be made to recent papers on plasma physics. A bibliography of papers on shock-tube work was published in 1956,[57] but there does not appear to be any such bibliography for papers in the other branches of high temperature physics.

Spectrum of Neutral Nitrogen

The ground state of the neutral nitrogen atom is $1s^2\ 2s^2\ 2p^3\ {}^4S_{3/2}{}^0$. The ionization potential is 14·54 volts, corresponding to a term value for the ground state of 117,345 cm.$^{-1}$; and the two metastable states ^{2}D and ^{2}P having the same electron configuration as the ground state lie respectively 19,200 cm.$^{-1}$ and 28,840 cm.$^{-1}$ above it.[6] The three valence electrons give rise to doublet and quartet terms.

Reference has already been made to some of the earlier work on measurement and classification of lines of N I, both in the visible and quartz ultra-violet[30, 31, 45, 48, 49] and in the vacuum ultra-violet regions,[46, 47] the results of which were analysed and compared with the iso-electronic spectra of C II, etc.[62–68] Much additional research was carried out around 1930,[69–77] including investigations of the metastable levels.[69, 70, 72–74] The results have been incorporated by Moore in the National Bureau of Standards 'Atomic Energy Levels', 1948.[6] This is based on the work of Duffendack and Wolfe[75] and of Ingram[76] in the infra-red to quartz ultra-violet regions and that of Ekefors[77] and Kamiyama[78–80] in the vacuum ultra-violet. Ninety terms are given. These arise from electron configurations in which one of the $3p$ electrons is raised to the states 3–12s, 3, 4p, and 3–12d. A few terms refer to states in which the $2p^2$ core is in the excited ^{1}D state instead of the normal ^{3}P state.

Additions to the National Bureau of Standards Tables were made in 1958 by Eriksson,[61] who measured or re-measured over 100 lines, mainly in the infra-red, and established five new terms. He also obtained improved values for certain old terms, from which he recalculated some vacuum ultra-violet wave-lengths.

Lists of wave-lengths may be found, both in the original papers and in Moore's Multiplet Tables,[7, 8] based on the same work as 'Atomic Energy Levels'.[6] Forty multiplets are given in the range 13,000 A.–3400 A.,[8] including 3 arising from forbidden transitions, and 13 multiplets in the quartz and vacuum ultra-violet regions,[7] of which 3 are transitions to the ground state and the remainder to the ^{2}P and ^{2}D metastable states.

Although transition probabilities have been calculated for several N I lines (see p. 444), no measurements appear to have been made of them. However, the continuous absorption coefficient of atomic nitrogen from its onset at 800 A. down to about 400 A. has been measured.[81] The maximum cross-section (at 650 A.) is found to be $14{\cdot}4 \times 10^{-18}$ cm.^{2}, in fair agreement with the calculated maximum of $10{\cdot}8 \times 10^{-18}$ cm.^{2} (see p. 444).

Spectrum of Ionized Nitrogen

A. SINGLY IONIZED

N II has the carbon-like ground state $1s^2\,2s^2\,2p^2\;{}^3P_0$. In 'Atomic Energy Levels'[6] the ionization potential is given as 29·605 volts, corresponding to a term value for the ground state of 238,846·7 cm.$^{-1}$, but in 1958 Eriksson[83] redetermined this limit as $238{,}750{\cdot}5 \pm 1{\cdot}3$ cm.$^{-1}$ The two valence electrons give rise to singlet and triplet systems. However, there are also several quintet terms arising from excitation of one of the $2s$ electrons.

Early measurements and classifications of N II lines[90–94] were analysed and compared with the iso-electronic spectra C I, O III, etc.[84–89] In 1934 Edlén[106] published a monograph on the lines and term values of the spectra N II, III, IV and V (together with those of other ions iso-electronic with these). As to N II his tables are based on the work of Fowler and Freeman[93, 94] with some additions of his own.[95, 96] The data in 'Atomic Energy Levels'[6] are taken from Edlén's monograph,[106] with corrections from a later paper of his.[97]

Fifty-eight terms of N II are listed in 'Atomic Energy Levels'. The electron configuration $1s^2\,2s^2\,2p^2$ of the ground state gives rise to three terms, of which the lowest is ^{3}P (with triplet separations of 49·1 cm.$^{-1}$ for $J=0$ to $J=1$ and 82·2 cm.$^{-1}$ for $J=1$ to $J=2$). The two metastable terms ^{1}D and ^{1}S are respectively 15,315·7 and 32,687 cm.$^{-1}$ above the ground state. Most of the other terms arise from electron configurations in which one of the $2p$ electrons is excited to one of the states 3–5s, 3,4p, 3–5d, 4–5f. The remainder, however, are built on the excited state $2s\,2p^2$ (^{4}P) of the ion; some of these are quintet terms, and three of them are above the ionization limit corresponding to the ground state of N III. 'Atomic Energy Levels' also lists observed g-values for twelve terms (see also p. 443).

The wave-lengths of 74 multiplets in the region 13,000 A. to 3400 A. (including 3 from forbidden transitions) and 23 multiplets in the ultra-violet region are to be found in Moore's Multiplet Tables.[7, 8] These have been compiled from the sources given above.

Important additions to the spectrum of N II were reported in 1958 by Eriksson.[83] He measured 450 lines, from which he derived 55 new levels. The configurations of which one or more terms are now known are:

$2s^2\,2p$: 3–6s, 3–4p, 3–5d, 4–7f, 5g

and

$2s\;2p^2$: 3s, 3p, 3d, 4–5f

In particular, Eriksson calculated from the $2s^2\,2p\;nf$ series a new value of 238,750·5 cm.$^{-1}$ for the series limit, and, by measuring a quintet–triplet intercombination line, succeeded for the first time in linking the quintet levels with the singlets and triplets.

Oscillator strengths of some N II lines have recently been determined experimentally and compared with calculated values.[82] The calculations are discussed on page 444.

B. DOUBLY IONIZED

N III has the boron-like ground state $1s^2\,2s^2\,2p\;{}^2P_{1/2}$, with an ionization potential of 47·426 volts, corresponding to a term value for the ground state of 382,625 cm.$^{-1}$.[6] Excitation of the $2p$ valence electron gives rise to a doublet spectrum. Quartet and doublet systems are associated with electron configurations in which one of the $2s$ electrons is excited.

Refs. p. 445

A number of N III lines were measured and classified by Bowen,[92] Freeman,[98] and Cady.[99] Edlén's 1934 monograph[106] incorporates their results and some of his own earlier work.[95, 96] The data in 'Atomic Energy Levels'[6] are taken from this monograph, supplemented by later results of Edlén's,[97] which yielded the improved value for the series limit quoted above and linked the quartet levels with the doublet system by means of intercombination lines.

Fifty seven terms of N III are listed in 'Atomic Energy Levels'.[6] The metastable $^2P_{3/2}$ term having the same electron configuration as the ground term is separated from it by 174·5 cm.$^{-1}$. The lowest excited terms arise from the configurations $2s\,2p^2$ and $2p^3$. Most of the other terms are built on the $2s^2\ ^1S_0$ ground state of the ion, with the valence electron in states 3–5*s*, 3,4*p*, 3–6*d*, 4–6*f*, 5,6*g*; the remainder, forming quartet-doublet systems, have the core configuration $2s\,2p$, and 13 of them are above the ionization limit (i.e., the ground state of N IV).

Wave-lengths of N III lines may be found, in addition to the original papers referred to above, in Moore's Multiplet Tables: 17 multiplets are listed in the region 13,000 A. to 3400 A. and 30 multiplets in the ultra-violet region.[7]

C. MORE HIGHLY IONIZED

N IV has the beryllium-like ground state $1s^2\,2s^2\ ^1S_0$, with an ionization potential of 77·450 volts, corresponding to a term value for the ground state of 624,851 cm.$^{-1}$.[6] The two valence electrons give singlet and triplet systems. The spectrum is less well known than those of N II and N III. A number of lines were measured and classified by Freeman[100] and Cady.[99] For this spectrum also Edlén's 1934 monograph[106] incorporates these earlier results with his own,[95, 96, 101, 102] 'Atomic Energy Levels'[6] being based on this monograph and Edlén's later paper[97]: 37 terms are listed, one above the ionization limit, from the configurations 2*s* plus 3*s*, 2–5*p*, 3–6*d*, 4*f*, 5*g*, and 2*p* plus 3*s*, 2–4*p*, 3*d*. Since no intercombination lines between singlets and triplets have been observed, there is some uncertainty about the absolute values of the singlet states. Moore's Multiplet Tables give the wave-lengths of 17 multiplets in the visible and infra-red regions[8] and 19 in the ultra-violet,[7] taken from the papers referred to above.

N V has the lithium-like ground state $1s^2\,2s\ ^2S_{1/2}$, with an ionization potential of 97·863 volts, corresponding to a term value for the ground state of 789,532·9 cm.$^{-1}$.[6] The spectrum consists of doublets. Edlén's 1934 monograph[106] is again the principal source, incorporating his own earlier results[95, 96, 103, 104] and those of Cady.[99] 'Atomic Energy Levels'[6] also makes use of later unpublished work of Edlén's. The 26 terms listed are for excited states of the 2*s* electron 3–8*s*, 2–8*p*, 3–8*d*, 6–8*f*, 6–8*g*; but most of those for which the principal quantum number is 6 or more have been calculated, not measured. Moore's Multiplet Tables list the measured wave-lengths of 12 multiplets in the infra-red and visible[8] regions and 6 in the ultra-violet.[7]

N VI has the helium-like ground state $1s^2\ ^1S_0$. Its ionization potential is 551·925 ± 0·062 volts (ground state term value 4,452,800 ± 500 cm.$^{-1}$).[6] The spectrum consists of singlets and triplets. Tyrén[107] has measured three singlets and one intercombination line, and other terms have been calculated from extrapolation formulæ along iso-electronic sequences by Robinson[105] and Edlén (unpublished). The six terms given in 'Atomic Energy Levels'[6] are from Tyrén's measurements[107] and Edlén's calculations.

N VII is a hydrogen-like ion. 'Atomic Energy Levels'[6] gives its ionization potential as 666·83 volts (ground term 5,379,860 cm.$^{-1}$). Tyrén[107] has observed the first line of the Lyman series. The three terms given in 'Atomic Energy Levels' are from calculations by Mach (unpublished).

Zeeman, Stark and Pressure Effects

The Zeeman effect for complex atoms is described in the text books, e.g.,[1–5] and a good general account is also given in the recent edition of *Handbuch der Physik*.[108] In N I measurements have been made on some red and infra-red lines, from which *g*-values have been found for several levels.[109, 110] *g*-Values have also been determined for some levels of N II.[111] In both spectra the measured *g*-values are compatible in most cases with the values to be expected from *L–S* coupling. The observed *g*-values of 12 terms of N II are quoted in 'Atomic Energy Levels .[6]

The Stark effect in nitrogen does not appear to have been studied.

Although nitrogen has been much used in experiments on pressure broadening and pressure shifts, it is usually its effect as a foreign gas on other spectra that has been studied. Accounts of pressure effects are to be found in text books,[112, 113] and a recent review article discusses both the theoretical and experimental aspects.[114] A few experiments on pressure shifts in nitrogen spectra have been carried out: some N I lines have been investigated,[115, 116] and the effect has been studied in some detail for a number of lines of N II[117, 118] and a few of N III.[118]

Hyperfine Structure and Nuclear Moments

Before the development of radio-frequency techniques, nuclear moments were determined by optical investigation of the hyperfine structure, although nuclear spins were also obtained from band spectra. Kopfermann[119] has given a very full account of the theoretical background and of the methods of both optical and radio-frequency spectroscopy, and Ramsey[120] has summarized the application of these methods to the determination of nuclear moments, giving tables of results up to 1952 and many references. Further information may be found in review articles on the applications in this connection of atomic beams[121] and microwave spectroscopy[122] and in a book on molecular and atomic beams.[144] The fitting of nuclear moments to the shell model of the nucleus has also been reviewed.[123] Magnetic moments for the nitrogen nuclei have been calculated on the basis of the shell model.[124]

Early attempts to discover hyperfine structure in the nitrogen spectrum were in fact unsuccessful,[125] although the spins $I=1$ for ^{14}N[129] and $I=\frac{1}{2}$ for ^{15}N[127, 128] were determined from the alternation of intensities in N_2 band spectra. The other nuclear moments for both isotopes have been found by the various radio-frequency methods. Hyperfine structure due to the isotope shift between ^{14}N and ^{15}N has, however, been measured in a few infra-red lines.[126] A description of this effect is given in Kopfermann's book[119] and in a review article.[143]

Ramsey[120, 144] gives for the ^{14}N nucleus the following values: I (nuclear spin) $=1$; μ (nuclear magnetic moment) $= +0{\cdot}40371 \pm 0{\cdot}00006$ nuclear magnetons; Q (nuclear quadrupole moment) $= +0{\cdot}02 \times 10^{-24}$ cm.^{2} For ^{15}N he gives: $I=\frac{1}{2}$; $\mu = -0{\cdot}28313 \pm 0{\cdot}00012$ nuclear magnetons. The nuclear magnetic moments were first determined by the molecular beam magnetic resonance method[130, 131] and later with greater precision by nuclear induction.[132, 133] Nuclear quadrupole interactions have been found from microwave measurements on the rotational spectra of molecules containing ^{14}N,[134–136] but the evaluation of Q from these entails calculating the quadrupole coupling constants. There is considerable uncertainty about such calculations,[122, 135] and values of Q between 0·01 and 0·03 are possible[135, 136]; a recent calculation, in fact, puts the value of Q as low as $+0.007 \times 10^{-24}$ cm.^{2} [137]

A microwave absorption method has also been used to measure the hyperfine structure of the ground state of ^{14}N due to the magnetic dipole interaction.[138] This interaction has very recently been further studied by means of a new development in radio-frequency resonance techniques known as optical orientation with spin exchange.[139, 140] The latest values of the hyperfine structure interaction constants thus found by Anderson, Pipkin and Baird in 1959[140] are $+10{\cdot}4509$ for ^{14}N and $-14{\cdot}6457$ for ^{15}N. They also obtained improved values for the nuclear gyromagnetic ratios relative to that of the proton. Taking the present accepted value for the latter,[120] their results yield for the nuclear magnetic moments of the nitrogen nuclei: $\mu_{14} = +0{\cdot}403482$ and $\mu_{15} = -0{\cdot}282994$ nuclear magnetons, as against the values quoted by Ramsey above. By combining measurements of hyperfine structures and nuclear moments for the two isotopes, the above authors[140] have also determined the so-called hyperfine anomaly, or Bohr–Weisskopf effect, in nitrogen. This effect arises

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from the distribution of the magnetic moment over a nucleus of finite size and is measured by the amount by which the ratio of the hyperfine structures of the two isotopes, divided by the ratio of their gyromagnetic ratios, differs from one.[119, 141, 142, 143] The hyperfine anomaly found is 0·000983 ± 0·000017 for the nitrogen isotopes.[140]

Calculations

The application of quantum mechanics to the determination of atomic wave functions, and hence of energy levels and transition probabilities, has been fully described by Condon and Shortley.[145] Hartree[146] in 1946 summarized the calculations carried out up to that date on the spectra of the light and certain heavy atoms for states of ionization up to the fourth. In the case of N I, analytical and self-consistent-field wave functions have been found for the ground state[147, 148]; and parameters have been listed for analytic functions for the ground and some excited states of N III, IV, V and VI.[149, 150] Since the publication of the above review article, Hartree and Hartree have determined self-consistent-field functions with exchange for the ground state configurations of N I and N^-,[151] and others have made calculations for the ground state configuration of N II.[152, 156] Intermediate coupling for certain N I configurations has been discussed.[157]

As regards transition probabilities, the main interest has been in certain forbidden lines of astrophysical importance. Oscillator strengths have been calculated by various methods for a few such lines in both the N I[153, 154, 206] and N II[155, 156] spectra. The experimental determination of oscillator strengths of some N II lines has already been referred to.[82]

The electron affinity of nitrogen has been investigated theoretically.[151, 158, 159] Since it appears to have a small negative value, the N^- ion is probably unstable.[151, 159]

Bates and Seaton[160] have calculated the continuous absorption cross-section of atomic nitrogen. They find a value of about 9×10^{-18} cm.^{2} at the series limit, with a low maximum at slightly shorter wave-length. The calculated cross-section agrees reasonably well with that measured by Ehler and Weissler,[81] although the theoretical curve lies a little below the experimental curve.

X-Ray Spectroscopy

Early work on the *X*-ray spectrum of nitrogen was mainly concerned with measurements of the *K* absorption edge,[161–167] the value of which was also calculated.[168] Measurements were also made on the wavelength of the *K*-series lines in emission.[166, 169–176] The region concerned is in the neighbourhood of 30 A. Wave-length limits were first determined from critical potentials; later, more accurate spectrographic methods were used, the 'grating' being a fatty acid crystal or, more generally, a ruled diffraction grating at grazing incidence. The methods of soft *X*-ray spectroscopy and some of the experimental data on nitrogen are described in a textbook by Compton and Allison[197] and in the 1957 edition of *Handbuch der Physik* by Tomboulian.[198] The latter gives as the best experimental value for the *K* edge 31·00 A. in emission and 30·99 A. in absorption. The most recent values for the wave-length of the $K\alpha$ line are all around 31·60 A.[171, 173, 176, 202, 205]

Attempts have been made to resolve fine structure in the $K\alpha$ line, which is about 0·2 A. wide, but these have been unsuccessful.[175, 176, 201, 202] Fine structure has, however, been resolved in emission and in absorption in the *K* edge of nitrogen, both in the gaseous form and in various compounds, especially BN.[107, 199, 200, 203–205] In the case of BN the structure is attributed to the electronic energy bands in the crystal lattice. A general discussion of this subject may be found in various monographs and review articles, e.g.[195, 196, 198]

A table of energy levels of all light elements calculated from *X*-ray frequencies has recently been published by Cauchois.[192]

A number of workers have measured the mass absorption coefficient of N_2 for soft *X*-rays.[178–182, 184, 185] Results are summarized in Compton and Allison's book.[197] High precision measurements of this coefficient have been applied to the analysis of organic matter.[187, 188] Other effects studied include fluorescence,[177] the excitation of *K* radiation in nitrogen by α-particles,[186] the Compton effect,[183] and the small-angle scattering of *X*-rays from N_2.[189–191]

A recent development in *X*-ray spectroscopy is the production of mesonic *X*-rays, i.e., *X*-rays from an atom in which the radiating electron is replaced by a meson. *K* radiation from π^- mesonic atoms has been produced in nitrogen and used to study the interaction between the meson and the nucleus.[193, 194]

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Astrophysics

The spectrum of atomic nitrogen is of considerable interest in astrophysics. Lines of various states of ionization have been identified in the spectra of many stars, novæ, and nebulæ. In addition, forbidden lines of atomic nitrogen are a significant feature of auroral spectra and appear also in the twilight glow. Study of these lines, particularly of their intensity relative to bands of molecular nitrogen, has yielded much information on the state of the upper atmosphere.

Wave-lengths of nitrogen lines of astrophysical interest have been tabulated by Moore.[230] Further references to the various nitrogen spectra, energy levels, wave-length determination, etc., may be found on pages 440–445.

The following account, concerned as it is with the spectrum of atomic nitrogen, gives an incomplete picture of the significance of nitrogen in astrophysics. Molecular nitrogen plays an important rôle in atmospheric phenomena; for example, bands of N_2 and N_2^+ are features of the spectra of auroræ and airglows. Compounds of nitrogen, notably CN, show absorption bands in the spectra of the cooler stars and in interstellar space.

(*a*) THE ATMOSPHERE

The most important source of lines of the atomic spectrum of nitrogen is the aurora. General accounts of the spectra of the airglow and the aurora, their excitation and interpretation, are given in various reports and review articles.[1, 2, 41, 70]

Lines attributed to atomic nitrogen were photographed by Vegard in the spectra of auroræ in the years around 1930.[8, 9, 10, 12] There followed a certain amount of controversy over the identification of a strong ultra-violet line with the forbidden N I line at 3467 A.[11, 13, 14, 15, 18] This line is due to a transition from the metastable ^2P state to the ground state ^4S, both states having the same electron configuration (see p. 440). The identification was later supported by more accurate wave-

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length measurements,[39, 40, 42] thus showing the existence in the upper atmosphere of nitrogen atoms in the metastable ^2P state during an aurora. At about the same time Kaplan and others showed that the 3467 A. line could be excited in the laboratory in the afterglow of a discharge in nitrogen under certain conditions, closely associated with the appearance of the forbidden Vegard–Kaplan bands of N_2.[3–7] In later laboratory experiments this phenomenon was studied further.[30–33, 45]

The forbidden doublet at 5198, 5200 A. due to the transition from the other metastable state, ^2D (see page 440), was identified by Dufay, Götz, and others in auroræ at low latitudes.[20, 21, 25, 26, 38] Recent reports of auroral spectra mention particularly the occurrence of this doublet at low latitudes and at very high altitudes.[55, 57–59] The mechanism of excitation of these forbidden lines has been discussed.[17, 22, 53] The life-times of the ^2P and ^2D states, particularly the latter, are so long that they can radiate only when the gas density is very low. Calculations of the transition probabilities of these lines have already been referred to (see page 444).

The attribution[27, 28] of other weak auroral lines to atomic nitrogen appeared at first to be more doubtful.[2, 43, 44] Various infra-red lines of N I have, however, been reported,[46–50, 52, 57] and the processes of emission of such lines have been studied in the laboratory.[34, 35] In recent years a large number of lines in the visible region have been identified by Vegard and others with various transitions, permitted and forbidden, in the spectra of both N I and N II.[51, 52, 54–58, 59]

It has been suggested that in the spectrum of the night sky certain radiations in the visible and near ultra-violet and infra-red regions may be due to atomic nitrogen,[16, 29, 36, 37] but it seems more likely that they are in fact N_2 bands.[2, 46] The 5200 A. doublet corresponding to the forbidden transition ^4S–^2D in N I has, however, been definitely observed in the twilight glow.[60–64]

The emission of the line spectrum of nitrogen from the upper atmosphere in certain conditions is, of course, of great interest in studies of the constitution of this region. The information that can be obtained about the dissociation of molecular nitrogen and the presence of N and N^+ in metastable states has been discussed in a number of papers.[1, 2, 19, 22–24, 27, 29, 47, 48, 50, 53, 59] Recent work on the airglow and aurora was reported at a symposium in 1955.[70]

The spectrum of lightning has been photographed from the ultra-violet to the near infra-red. Throughout these regions lines of N I and N II have been identified.[65–69]

(*b*) SUN, STARS, NEBULÆ, ETC.

Nitrogen is a common constituent of the universe, and so lines of nitrogen in various degrees of ionization are found very widely in absorption and in emission. Merrill has published tables showing the lines of every element that are to be found in the spectra of different types of stars, nebulæ, etc.[71] The new (1958–59) edition of *Handbuch der Physik*[232] contains many good general articles covering the spectroscopic aspects of astrophysics, with extensive references.

Although the existence of nitrogen in the sun was at first in doubt,[72, 73] it has actually been shown that nitrogen is one of the most abundant constituents,[74, 75] being identified by means of lines in the infra-red region.[75, 76] The possibility that two infra-red lines in the 10,400 A. region represent the forbidden transition between the ^2P and ^2D metastable states of N I (see page 440) has been discussed.[77–79] Calculations have been made on the way in which the far ultra-violet emission spectrum of the corona is affected by the K X-ray absorption edge of nitrogen[80] (see page 444) and on the contribution of radiation from highly ionized nitrogen atoms to the ultra-violet emission from the chromosphere.[81]

As regards meteors, N I lines have been identified in the spectra of Perseid meteors.[82]

The spectra of nebulæ and novæ contain many lines of N I, II, and III. Forbidden lines of N II are especially characteristic of nebulæ; owing to the extremely low gas density, metastable states of long lifetime are not destroyed by collisions. Calculations of the oscillator strengths of such lines are referred to on page 444. Accurate

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wavelengths for N I, II and III lines occurring in stellar and nebular spectra have been given[84, 87, 231] and also the conditions for their excitation, with reference to the measured intensity ratios.[83, 85, 92] The lines found in the spectra of particular nebulæ[93, 98, 109, 110, 122] and double galaxies[86] have been discussed. The forbidden N II lines and certain other nitrogen lines are prominent in the spectra of planetary nebulæ[88, 89, 97–107] and their relative intensities have been used to determine the spatial structure and chemical composition of these nebulæ.[89, 95, 97, 99, 100, 103, 106, 107] The spectra of the stars forming the nuclei of the planetary nebulæ are found to contain lines of higher states of ionization of nitrogen.[88, 94, 96, 100, 102]

Lines of N II and N III, both permitted and forbidden, appear in the spectra of novæ at certain periods in their existence[83, 84, 90, 91] and have also been identified in a supernova.[108] Novæ particularly thoroughly studied in this respect over periods of years include T. Coronæ Borealis,[111–118] Aquilæ,[119–121, 134] Herculis,[123–129, 135] Serpentis,[133, 135–139] and Cygni,[130–134, 148] and a considerable amount of work has also been done on nitrogen lines in the spectra of other novæ.[140–152]

Absorption or emission lines of N I, II and III, permitted and forbidden, have been reported in a large number of stellar spectra besides those of novae. In the hotter stars, e.g., Wolf-Rayet stars, lines of N IV and N V appear. In some cases the intensities and widths of the nitrogen and other lines have been used to estimate relative abundances, temperatures, electron pressures, etc. Details of these spectra will not be given in this account; the large number of papers on the subject may be grouped roughly as follows:

Features peculiar to stars of early spectral type[153–159];

Wolf-Rayet stars[160–170];

Variable stars in which the behaviour of nitrogen lines is of interest:

Z. Andromedæ[171–176]
γ-Cassiopeiæ[177–179]
γ-Pegasi[180–182]
A G Pegasi[183–186]
P. Cygni and other stars of same type[187–190]
Others[191–201];

Other stars, conditions of radiation, etc.[202–229]

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THE SPECTROSCOPY OF MOLECULAR NITROGEN AND CERTAIN NITROGEN COMPOUNDS

BY R. F. BARROW AND A. J. MERER

The Spectrum of Gaseous Nitrogen

The study of the spectrum of molecular nitrogen, some band-systems of which may be readily excited in simple electrical discharges,[8, 10] played an important part in the development of the interpretation of band spectra. In early work, the effects of magnetic fields[1, 2] and of electric fields[4] both on the luminous discharge and on the spectral lines were examined, and searches were made for regularities among the band lines.[3, 5, 9, 12, 13, 20] The Doppler effect[7] was also studied, with the primary object of identifying[6, 8] the emitting species. The characteristic difference between the multiplicities of the states of N_2 (singlets, triplets, . . .) and those of N_2^+ (doublets, quartets, . . .) provided a link between atomic and molecular spectra,[11] and the alternating intensities of the band lines[14, 17] (since $^{14}N_2$ is a homonuclear molecule with $i \neq 0$) enabled the bands of N_2 and of N_2^+ to be distinguished from those of common impurities, such as NO. There were also early investigations of the spectrum in the Schumann region[15, 16, 18]—a region by no means exhausted at the present time.[24] There followed the application of the theory of molecular spectra, initiated by Hund, to the interpretation of these results.[19, 21–23]

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EXCITATION

Band systems of N_2 and of N_2^+ may be excited in a variety of different ways. Much work has been done on excitation by electron impact,[1–27] often with the object of determining excitation potentials. More reliable values have since been obtained from spectroscopic studies of the energy levels. Other experiments on the excitation of these spectra have been described.[28–83] Among the sources examined are conventional discharge tubes,[36, 49, 58, 59] high-frequency electrodeless discharges,[38, 41, 42, 47, 57, 63, 64, 66] ozonizer discharges,[61, 77–79] low-voltage arcs,[35, 39, 51, 68] high-voltage arcs[72, 76] and sparks[74, 81] and discharges excited by microwaves[82, 83] (see also references 95–100).

Excitation by impact of particles, other than electrons, has also been examined.[84–88, 93] The spectrum of air, excited by a proton beam, is strikingly similar to that of the aurora[85, 87] (see p. 467). The effects of D^+, He^+ and Ne^+ have also been studied; emissions from the ions N^+ and N_2^+ were found to be independent of the speeds of the particles, but strongly dependent on the kind of particle.[86]

Observations of fluorescence spectra have been reported[89–92]; the experimental difficulties are considerable since wave-lengths in the Schumann region are required for excitation. A feeble luminosity which accompanies the slow thermal decomposition of some azides appears to consist[94] of bands of the Vegard–Kaplan system of N_2 (see p. 460). Studies have also been made of the Stark[101, 102] and Faraday[103] effects, and of photo-ionization.[104]

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EFFECTS OF FOREIGN GASES

A number of qualitative observations of the effects of foreign gases on the emission spectrum have been made.[1–11] Experimentally, some of these effects are highly important; for example, the forbidden Vegard–Kaplan bands, A $^3\Sigma_u^+ - \mathrm{X}\ ^1\Sigma_g^+$, are observed with considerable intensity in a spectrum excited in xenon at 1 atmosphere pressure containing a very small amount of nitrogen.[8] The production of nitrogen atoms by reaction of excited krypton atoms with nitrogen molecules has been discussed.[10]

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ELECTRONIC STATES AND SPECTRUM

A large number of electronic states of the nitrogen molecule is known[105]. They are listed in Table I, which, with very few alterations, is condensed from a table given by Mulliken.[64] Mulliken's table also includes predictions about a number of states, some stable and some repulsive, for which experimental information is not yet available. The ground state of N_2 may be written $KK\,\sigma_g^2\,\sigma_u^2\,\Pi_u^4\,\sigma_g^2$, $^1\Sigma_g^+$, and the lowest excited states are formed by promoting an electron into one of the higher, anti-bonding, molecular orbitals $1\Pi_g$ or $3\sigma_u$. The excited configuration $\ldots\,\sigma_g^2\,\sigma_u^2\,\Pi_u^3\,\sigma_g^2\Pi_g$ (represented in Table I by 2 2 3 2 1 0) gives rise to six electronic states, and it is an indication of the degree of completeness of the studies of this spectrum that there is now available experimental information about five of these states. They are [2] A $^3\Sigma_u^+$, [6] $a^1\ ^1\Sigma_u^-$, [7] $\mathrm{B}^1\ ^3\Sigma_u^-$, [8] $\omega\ ^1\Delta_u$, [30] $b^1\ ^1\Sigma_u^+$: the exception is the predicted state [4] $^3\Delta_u$ which has not yet been observed. Similarly, the other low-lying configuration $\ldots\,\sigma_g^2\,\sigma_u^2\,\Pi_u^4\,\sigma_g\,\Pi_u$ gives $^3\Pi_g$ and $^1\Pi_g$, and these are very plausibly identified with the states [3] B $^3\Pi_g$ and [5] $a\ ^1\Pi_g$. Another low-lying state of importance is [9] $^5\Sigma_g^+$. This state has a very shallow minimum—perhaps[74] about 850 cm.$^{-1}$: it predissociates[53] states [3] and [5], and is of importance in connexion with the mechanism of the Lewis–Rayleigh afterglow.

A summary of the observed transitions between the states is given in Table II. In addition to the bands which have been analysed, there is a large number whose analysis is incomplete or whose identity has not yet been determined (see, for example,[39, 42, 77, 80, 81, 85, 109]).

The best present values for the constants of the ground state of the molecule result from the rotational analysis of the Lyman–Birge–Hopfield system,[65, 77] combined with measurements of the rotational and vibrational Raman spectra.[78] The results are as follow:

$$G_v = 2358{\cdot}07(v+\tfrac{1}{2}) - 14{\cdot}188(v+\tfrac{1}{2})^2 - 0{\cdot}0124(v+\tfrac{1}{2})^3$$
$$B_v = 1{\cdot}9987 - 0{\cdot}01781(v+\tfrac{1}{2})$$
$$r_e = 1{\cdot}0976\ \text{A.}$$

The dissociation energy, D_0, is now known[72, 79] to be 9·758 ± 0·005 ev., or 78,717 ± 40 cm.$^{-1}$, equivalent to 225·0$_4$ ± 0·01 kcal. mole^{-1}. This value is based[64] on $\nu_{00}[2]-[1]+\nu_{00}[3]-[2], +\nu_{00}[11]-[3]$ plus the predissociation energy of [11] C $^3\Pi_u$ into N(^4S) + N(^2D) which[24] is 8960 ± 40 cm.$^{-1}$ (for earlier discussions, see refs. 86–94). Other predissociations are summarized in Mulliken's table[64]; see also refs. 95–101.

Three Rydberg series are known, (i) the Worley–Jenkins series, converging on X $^2\Sigma^+$ of N_2^+, (ii) Worley's third series, converging on $v=1$ of A $^2\Pi_{1/2}$ and (iii) the Hopfield series, which converges on B $^2\Sigma^+$. The 0–0 band-heads are represented by the following equations:

$$\text{(i) X–X:}\quad \nu_m = 125{,}666 - R/[m + 0{\cdot}3450 - 0{\cdot}1000/m - 0{\cdot}100/m^2]^2$$
$$m = 2, 3, \ldots 26$$
$$\text{(ii) A–X:}\quad \nu_m = 136{,}607 - R/[m - 0{\cdot}0441 - 0{\cdot}018/m]^2$$
$$m = 2, 3, \ldots 6$$
$$\text{(iii) B–X:}\quad \nu_m = 151{,}240 - R/[m - 0{\cdot}092]^2$$
$$m = 3, 4, \ldots 10$$
$$R = 109{,}735\ \text{cm.}^{-1}$$

Table I.—Electronic States of the Nitrogen Molecule

	State	Probable electron configuration[a]	T_{00}	ω_e	$x_e\omega_e$	B_0	$10^2\alpha$	r_e
95	[$^1\Sigma_u^+$]	2 2 4 1 0 0; $7p\sigma_u$	121,767	[2177]				
94	v		121,247	925*				
93	$u\ ^1\Sigma_u^+$		120,585	547	7	1·07		1·50*
92	[$^1\Sigma_u^+$]	2 1 4 2 0 0; $3s\sigma_g$	[120,000]	[2450]				[1·07]
91	[$^1\Sigma_u^+$]	2 2 4 1 0 0; $6p\sigma_u$	119,738	2179*				
90	t		118,487	482*		1·16		1·44*
89	[$^1\Sigma_g^+$]	2 2 3 2 0 0; $3p\pi_u$		[1910]				[1·17]
88	($z\ ^1\Delta_g$)	2 2 3 2 0 0; $3p\pi_u$	(115,355)	(1700)		1·753	1·5	1·16
62–87			117,000	repulsive, or loosely bound states				
61	$y\ ^1\Pi_g$	2 2 3 2 0 0; $4p\sigma_u$	114,165·2	1707·8*		1·781		1·16*
60	s		116,683	522*		1·11		1·47*
59	[$^3\Sigma_g^-$]	2 2 3 2 0 0; $3p\pi_g$		[1910]				[1·17]
58	$x\ ^1\Sigma_g^-$	2 2 3 2 0 0; $3p\pi_u$	113,211·0	1916·0	20·7	1·739	2·25	
57	[$^3\Pi_g$]	2 2 3 2 0 0; $4p\sigma_u$		[1900]				[1·16]
56	[$^3\Delta_g$]	2 2 3 2 0 0; $3p\pi_u$		[1910]				[1·17]
55	[$^3\Sigma_g^+$]	2 2 3 2 0 0; $3p\pi_u$		[1910]				[1·17]
54	$e(e^1)[^1\Sigma_u^+]$	2 2 4 1 0 0; $5p\sigma_u$	115,564	2180*				
53	$h\ ^1\Sigma_u^+$	(2 2 3 2 0 0; $4d\sigma_g$?)	112,769·5			1·655		1·20*
52	$r\ ^1\Sigma_u^+$		110,944	(640)		(1·07)		(1·50)
51	$s'\ ^1\Sigma_u^+$		110,658·3			1·595		1·23*
50	f		110,190					
49	$q\ ^1\Sigma_u^+$	(2 2 3 0 3 0)	109,833	715	9	1·12	(2)	1·46
48	$^1\Pi_g$	[2 2 3 2 0 1]	?		? repulsive			
47	$g\ ^1\Sigma_u^+$		108,950			1·356		1·33*
46	($d'\ ^1\Pi_u$)	(2 2 4 1 0 0; $3p\pi_u$)	(108,698)			(1·797)		(1·16*)
45	$k\ ^1\Sigma_u^+$		108,547			1·435		1·30*
44	$p\ ^1\Pi_u$	(2 2 3 1 2 0)	108,372	749*				1·41*
40–43		$^5\Sigma_g^-$, $^5\Pi_u$, $^5\Sigma_u^-$, $^5\Pi_g$	107,500		repulsive			
39	[$^3\Pi_u$]	[2 2 3 1 2 0]	[104,000]		? repulsive			

Table I.—(continued)

	State	Probable electron configuration	T_{00}	ω_e	$x_e\omega_e$	B_0	$10^2\alpha$	r_e
38	$[^3\Sigma_g]$	[2 2 4 0 2 0]	[(107,758)]		re	pulsive		
37	$[^3\Pi_g]$	[2 2 3 2 0 1]	?		re	pulsive		
36	$\{[^3\Pi_u]$ $r'\ {}^1\Sigma_u^+$	[2 2 4 1 0 0; $3p\pi_u$]	106,370			1·711		1·19*
35	$0(0^1)(^1\Pi_u)$	2 2 3 2 0 0; $3s\sigma_g$	105,690	(2020·0)	(32·3)	1·694		1·19*
34	$m(q^1)\ {}^1\Pi_u$	(2 2 3 1 2 0)	105,348	764*		1·361		1·33*
33	$d\ {}^1?_u$		104,718					
32	$p'(c)\ {}^1\Sigma_u^+$	2 2 4 1 0 0; $4p\sigma_u$	104,324	(2217)	(19)	1·929		1·12*
31	$l\ {}^1\Pi_u$	(2 2 4 0 1 1)	104,141			1·494		1·27*
30	$b'\ {}^1\Sigma_u^+$	(2 2 3 2 1 0)	103,672	751·64	4·82	1·152	0·48	1·444
29	$[^3\Pi_u]$	[2 2 3 2 0 0; $3s\sigma_g$]	[(103,000)]	[1950]				[1·18]
28	$D\ {}^3\Sigma_u^+$	2 2 4 1 0 0; $4p\sigma_u$	101,873			1·96		1·108*
27	$b\ {}^1\Pi_u$		101,456	698*		(1·41)		(1·31)
26	$j\ {}^1\Sigma_u^+$	(2 2 4 1 0 1)	100,821			1·46		1·28*
25	$i\ {}^1?_u$		(98,486)	670*				
24	$[^1\Sigma_g^+]$	[2 2 4 1 0 0; $3s\sigma_g$]	[(98,300)]	[2215]		[1·92]		[1·12]
23	$[^1\Pi_u]$	[2 1 4 2 1 0]	[(98,000)]	[2035]		[1·82]		[1·15]
18–22		$^5\Sigma_g^+,\ {}^5\Delta_g,\ {}^5\Pi_g,$ $^5\Sigma_u^+,\ {}^5\Delta_u$	98,000		re	pulsive		
17	$[^3\Delta_g]$	[2 2 3 1 1 1]	[97,944]		re	pulsive		
16	$[^3\Sigma_g^+]$	[2 2 3 1 1 1]	[97,944]		re	pulsive		
15	$^3\Pi_u$	2 2 4 0 1 1	(94,000)					*f*
14	$[^5\Pi_u]$	{2 2 3 1 2 0 2 2 2 2 1 1^+	[(97,400)]		? re	pulsive		
13	$c^1\ {}^3\Pi_u$		97,583					1·37
12	$E\ (^3\Sigma_g^+)$	2 2 4 1 0 0; $3s\sigma_g$	95,770	2184·5*				[1·12]
11	$C\ {}^3\Pi_u$	2 1 4 2 1 0	87,984	2035·1	17·08	1·8160	1·97	1·148 *g*
10	$[^7\Sigma_u^+]$	[2 2 2 1 2 1]	[78,718]		re	pulsive		
9	$^5\Sigma_g^+$	{2 2 2 2 2 0 2 2 3 1 1 1						*e*
8	$\omega\ {}^1\Delta_u$	2 2 3 2 1 0	71,697·7	1548	8	1·490	1·66	1·2
7	$B\ {}^1(\gamma)^3\Sigma_u^-$	2 2 3 2 1 0	65,850·6	1517·7	12·2	1·464	1·61	1·279
6	$a'\ {}^1\Sigma_u^-$	2 2 3 2 1 0	67,738·2	1530·0	12·0	1·472	1·64	
5	$a\ {}'\Pi_g$	2 2 4 1 1 0	68,951·2	1694·1	13·9	1·607	1·78	*d*
4	$[^3\Delta_u]$	[2 2 3 2 1 0]	[59,000]	[1490]				1·25 *c, g*
3	$B\ {}^3\Pi_g$	2 2 4 1 1 0	59,314	1734·11	14·47	1·6288	1·84	*g*
2	$A\ {}^3\Sigma_u^+$	2 2 3 2 1 0	49,757	1460·37	13·89	1·433	1·3	
1	$X\ {}^1\Sigma_g^+$	2 2 4 2 0 0	0	2358·07	14·19			

Notes:

a. Probable electron configurations are taken from Mulliken.[64] The numerals represent numbers of electrons in the various molecular orbitals, in order

$$\ldots 2\sigma_g\ 2\sigma_u\ 1\pi_u\ 3\sigma_g\ 1\pi_g\ 3\sigma_u$$

so that, for example, 2 2 3 2 0 1 stands for

$$KK\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^3\ (3\sigma_g)^2\ (1\pi_g)^0\ (3\sigma_u)^1$$

b. Square brackets [ ] indicate predicted[64] values: uncertain values are given in parentheses ( ). Asterisks above values of ω_e or of r_e indicate that these are values of $\Delta G_{1/2}$ or of r_0 respectively.

c. See references 64, 74.

d. For the character of [5], $^1\Pi_g$ and not $^1\Pi_u$, see references 48, 66.

e. See references 53, 74.

f. This state is known only through its effects in predissociating state [11].[24, 64]

g. Values of $W = 2A\Lambda S$ are:

State [3] +84·6 cm.$^{-4}$
[4] [+85]
[11] +78·0

h. For potential energy–distance curves for some of the lower states and also for more highly excited states, see references 107 and 108, respectively.

Table II.—Band Systems of the Nitrogen Molecule

Transition	Absorption or Emission	Remarks	References
2–1	A	Vegard-Kaplan system, intensity $2{\cdot}5 \times 10^{-6}$ of typical allowed transition	73
2–1	E		45, 47
3–2	E	First Positive system	4, 9, 11, 12, 20, 22, 42, 50, 54, 55, 58
5–1	A	Lyman–Birge–Hopfield system, intensity $4{\cdot}6 \times 10^{-4}$ of typical allowed transition	65, 66
5–1	E		1, 2, 5, 6, 7, 10, 19, 35, 42, 48, 59, 61, 77
6–1	A	intensity $3{\cdot}0 \times 10^{-6}$ of typical allowed transition	72
6–1	E		75, 82
7–1	A	intensity $1{\cdot}5 \times 10^{-6}$ of typical allowed transition	76
7–1	E		75, 82
7–3	E	γ bands	56, 67–70, 102, 103
11–1	A	intensity $1{\cdot}7 \times 10^{-4}$ of typical allowed transition	59
11–3	E	Second Positive system	13, 22–27, 32, 47, 51, 106
12–2	E	Herman–Kaplan bands	17, 42, 43, 64
13–3	E	Goldstein–Kaplan bands	16, 39, 71
25–1	A		37, 38
26–1	A		37, 38
27–1	A	Birge–Hopfield bands: strong system	37, 38
27–1	E		7
28–3	E	Fourth Positive system	31
30–1	A	strong system	37, 38
30–1	E		7, 19, 28, 49, 61
31–1	A		37, 38
31–5	E		42, 46
32–1	A	first member of X–X Rydberg series	37, 38, 64
32–5	E		40, 41, 47, 49, 62
33–5	E		42, 47
34–1	A		37, 38, 41
34–5	E		40–42, 47, 52, 62
35–1	A	first member of A–X Rydberg series	57, 64
35–5	E		52
36–5	E		40, 41, 62, 64
44–1	A		37, 38
45–5	E		62
46–5	E		52
47–1	E		19
47–5	E		62
49–1	A		37, 38
50–1	A		37, 38
50–1	E		19
51–5	E		40, 62
52–1	A		37, 38
53–1	A		37, 38
53–1	E		19
53–5	E		36, 40–42, 62
54–1	A	X–X Rydberg series	37, 38, 64
54–5	E		42–44
58–6	E	Fifth Positive system	3, 10, 21, 40, 43, 44, 60, 72, 104
60–1	A		37, 38
61–6	E	Kaplan's first system	3, 14, 15, 17, 40, 42–44, 63, 72
61–8	E	Kaplan's second system	14, 15, 17, 42–44, 63, 72

Table 2.—(continued)

Transition	Absorption or Emission	Remarks	References
88–8	E		62
90–1	A		37, 38
93–1	A		37, 38
94–1	A		37, 38
(94–49)	E		83
Rydberg series			
X–X	A	Worley–Jenkins Rydberg series	30, 33, 34, 37, 38, 64
A–X	A	Worley's third Rydberg series	57, 64
B–X	A	Hopfield's Rydberg series	8, 18, 29, 64

Mulliken[64] bases the terms of N_2^+ on the Worley–Jenkins limit, taken to be 125,672 cm.$^{-1}$. This is the value for the first ionization potential of nitrogen, N_2, and is equivalent to 15·58 ev. The series are considered[64] to be respectively:

$$\text{X–X:}\quad KK\,\sigma_g^2\,\sigma_u^2\,\Pi_u^4\,\sigma_g,\ np\sigma_u,\ {}^1\Sigma_u^+$$

$$\text{A–X:}\quad KK\,\sigma_g^2\,\sigma_u^2\,\Pi_u^3\,\sigma_g^2,\ ns\sigma_g,\ {}^1\Pi_u$$

$$\text{B–X:}\quad KK\,\sigma_g^2\,\sigma_u\,\Pi_u^4\,\sigma_g^2,\ ns\sigma_g,\ {}^1\Sigma_u^+$$

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It had been suggested that some bands observed in emission from the solid products from gas discharges trapped at liquid helium temperatures were to be assigned[1, 2] to the transition $^5\Sigma - A\ ^3\Sigma_u^+$ in N_2. Isotopic substitution has now shown[3] that these bands arise from $A\ ^3\Sigma_u^+ - X\ ^3\Sigma_g^-$ in O_2. Emission, under certain conditions, of bands of the Vegard–Kaplan system of N_2, $A\ ^3\Sigma_u^+ - X\ ^1\Sigma_g^+$, is however, confirmed.[3]

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The Spectrum of the Nitrogen Molecule Ion, N_2^+

As in the case of N_2, the spectrum of N_2^+ was of importance in the early development of band spectroscopy.[4, 7, 10] Five electronic states of the molecule-ion are at present known and all the allowed transitions between these states have been observed. Details of the states and of the transitions are given in Tables III and IV below.

The intensity alternation in the rotational lines has been studied in the transition $B\ ^2\Sigma_u^+ - X\ ^2\Sigma_g^+$, both for[1, 5, 9] $(^{14}N_2)^+$ and for[25, 27] $(^{15}N_2)^+$. The ^{14}N nucleus has a spin of 1 and obeys Bose–Einstein statistics, the ^{15}N nucleus has a spin of $\frac{1}{2}$, and obeys Fermi–Dirac statistics.

Attempts have been made to measure the excitation potential for the B–X system by electron impact.[8] The best value at present available comes from the spectroscopically determined ionization potential of N_2 (see p. 461). The dissociation energy of $N_2^+(X\ ^2\Sigma_g^+)$ is then related to the dissociation energy of N_2 thus:

$$\begin{aligned} D_0 &= D_0(N_2) + \text{i.p.}(N) - \text{i.p.}(N_2) \\ &= 9{\cdot}758 + 14{\cdot}54 - 15{\cdot}58_0 \\ &= 8{\cdot}71_8 \text{ ev. or } 201{\cdot}_0 \text{ kcal./mole} \end{aligned}$$

Thus the dissociation energy of N_2^+ is only about 10% less than that of N_2 (see also ref. 23).

The first excited state in N_2^+, $A\ ^2\Pi_u$, for many years known only through its effects in perturbing[12, 14, 15, 17–20] the levels of the state $B\ ^2\Sigma_u^+$, was first observed directly in the transition A–X in auroral spectra.[31] Phenomena arising from the $A\ ^2\Pi_u$, $B\ ^2\Sigma_u^+$ perturbations are observed also in the Zeeman effect.[13] However no Stark effect is observed, only a reduction in band intensity with increasing electric field.[22] In a rather different way, there is strong interaction[52, 54] between the levels $B\ ^2\Sigma_u^+$ and $C\ ^2\Sigma_u^+$, so that the potential curves (see also ref. 50) for both states are unusual, and the course of the rotational and vibrational constants with vibrational quantum number is anomalous.[35, 48]

The absolute intensity of the $B\ ^2\Sigma_u^+ - X\ ^2\Sigma_g^+$ transition has been calculated[29, 30] as $f = 0{\cdot}18$. This is about five times larger than the experimental value,[49] $f = 0{\cdot}0348 \pm 0{\cdot}002$, which corresponds to a lifetime of the $B\ ^2\Sigma_u^+$ state of $(6{\cdot}58 \pm 0{\cdot}35) \times 10^{-8}$ sec. Relative transition probabilities have been calculated for the B–X system[36] and for the A–X system.[41]

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Excitation of the B–X system in the high frequency torch[43] and by electronic[44, 45] and ionic[44] impact has been studied. In excitation by an electron beam[45] the reaction:

$$e^- + \mathrm{N_2}(\mathrm{X}\ {}^1\Sigma_g{}^+) \rightarrow \mathrm{N_2}^+(\mathrm{B}\ {}^2\Sigma_u{}^+) + 2e^-$$

appears to be the most important mechanism for populating the B $^2\Sigma_u{}^+$ state. Measurements of relative band intensities[44] in the B–X and A–X systems excited by low-energy particles indicate that they depart considerably from the predictions of the Franck–Condon principle. In the A–X system, a significant variation of the electronic transition moment with internuclear distance has been found.

Table III.—Electronic States of the Nitrogen Molecule Ion, $\mathrm{N_2}^+$

State	Probable electron configuration $\ldots 2\sigma_g\ 2\sigma_u\ 1\pi_u\ 3\sigma_g\ 1\pi_g$	T_{00}, above $\mathrm{X}^1\Sigma_g{}^+$ in $\mathrm{N_2}$	Probable Dissociation products
184–191	various	[196 000]	$[{}^4S+{}^3P]$
183 $\mathrm{C}^2\Sigma_u{}^+$	2 2 3 1 1	190 214	excited products
182 $[{}^4\Delta_u]$	2 2 3 1 1	[190 000]	$[{}^2D+{}^3P]$
$\mathrm{D}({}^2\Pi_g)$	(2 3 4 0 1)	177 319	$[{}^4S+{}^3P]$
181 $[{}^4\Sigma_u{}^+]$	2 2 3 1 1	[175 000]	$[{}^2D+{}^3P]$
180 $\mathrm{B}^2\Sigma_u{}^+$	2 1 4 2 0	151 238	$^4S+{}^3P$
150 $\mathrm{A}^2\Pi_u$	2 2 3 2 0	134 688	$^4S+{}^3P$
100 $\mathrm{X}^2\Sigma_g{}^+$	2 2 4 1 0	125 672	$^4S+{}^3P$

State	T_{00}	ω_e	$x_e\omega_e$	B_e	α_e	r_e A.
$\mathrm{C}^2\Sigma_u{}^+$	64542·0	2072·$_5$	—	1·509*	—	1·263*
$\mathrm{D}({}^2\Pi_g)$	51647	905·5	11·69	—	—	—
$\mathrm{B}^2\Sigma_u{}^+$	25566·0	2371·5*	—	2·073*	—	1·075
$\mathrm{A}^2\Pi_u$	9016·5	1902·84	14·91	1·722	0·018	1·177
$\mathrm{X}^2\Sigma_g{}^+$	0	2207·19	16·14	1·932$_2$	0·020$_2$	1·116$_2$

Notes:

(i) An asterisk indicates a value of $\Delta G_{\frac{1}{2}}$, B_0 or of r_0.

(ii) Values of T_{00} above $\mathrm{X}^1\Sigma_g{}^+$ in $\mathrm{N_2}$ are based[52] on the limit of the Worley–Jenkins Rydberg series in $\mathrm{N_2}$.

(iii) The state D, observed in the transition D–A does not appear in Mulliken's tables.[52] However, a state with very similar properties is known in the spectrum of CN, where rotational analysis shows it to have the character $^2\Pi_i$ (near case *b*).[53]

Table IV.—Band Systems of the Nitrogen Molecule Ion, $\mathrm{N_2}^+$

Transition	Bands	References
150–100	Meinel bands	31–33, 37, 38, 51
180–100	First negative bands	1, 2, 3, 5, 6, 11–15, 17–21, 24, 25, 27, 35
183–100	Second negative bands	16, 26, 28, 34, 39, 40, 42, 48
D–150		46, 55

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Nitrogen Spectra of Various Origins

LIQUID NITROGEN

Liquid nitrogen is transparent[1] in the range 6500 A. down to 2000 A., and the gas does not absorb appreciably[2] until much shorter wave-lengths, in the region of the forbidden Lyman–Birge–Hopfield bands, which extend to 1130 A., and the bands of the C $^3\Pi_u$–X $^1\Sigma_g^+$ system in the region 1075 to 1130 A. Comparatively high values of extinction coefficients reported[3] for this region appear to be erroneous.[2, 4] Rough values of k (where k is defined by $I = I_0 \exp(-kx)$, with x the path length in cm. for gas at N.T.P.) are 0·1 cm.$^{-1}$ at the band-heads, and $<0{\cdot}01$ cm.$^{-1}$ between bands.

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There is no evidence of continuous absorption at wave-lengths above 850 A. Observations at still shorter wave-lengths, of astrophysical importance, have been reported[5–12] and discussed.[12]

At higher pressures, above 500 kg./cm.^{2}, continuous absorption[13] has been observed at wave-lengths between 2000 and 3000 A.

The participation of nitrogen in photochemical reactions[14, 15] has been reported, and ammonia and hydrazine are formed from N_2–H_2–Kr mixtures but probably by reaction[15] with excited krypton atoms.

Attempts to observe absorption from metastable nitrogen molecules have not been successful.[16]

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SOLID NITROGEN

The problem of the interpretation of the auroral spectrum prompted a number of investigations into the luminescence of solid nitrogen, excited for the most part by electron bombardment.[1–26] This spectrum contains bands of the first, second and fourth positive systems,[22] together with the Vegard–Kaplan bands.[24]

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THE NIGHT SKY

Molecular emission from nitrogen is observed in the light of the night sky.[1–32] The 0–0 band of the first positive system of N_2 in the infra-red is particularly strong,[5, 7, 8, 19, 20] and in some circumstances particularly during magnetic storms,[13, 29] at dawn,[15–17] or at twilight[13, 16, 17, 27] the first negative system of N_2^+ is also observed. Consideration has been given to the possibility of emission of a number of other systems[2, 6, 12, 23, 33, 34]: among these, the Vegard–Kaplan bands[9, 12, 14, 24, 31] and the system[32] $B^1(\gamma)\ ^3\Sigma_u^- - B\ ^3\Pi_g$ appear to be present.

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AURORA

Spectra of the aurora[1–47] are similar in many respects to those of the night sky. There are present, apart from lines of atomic oxygen and nitrogen and bands arising from O_2, a number of bands of molecular nitrogen, including those of the first and second positive systems and the Vegard–Kaplan bands of N_2, and the negative system of N_2^+. In the infra-red part of the spectrum, the predicted transition A $^2\Pi_u$–X $^2\Sigma_g^+$ in N_2^+ was identified for the first time from auroral spectra by Meinel.[29, 31]

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The study of these spectra provides important information about the conditions obtaining in the upper atmosphere[25] and problems of the mechanisms of excitation have been considered in some detail.[48–59]

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LIGHTNING

The second positive bands of N_2 are observed in the spectrum of lightning,[1, 2] and the negative system of N_2^+ is strong; NH bands are also observed.

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COMETS

The spectra of comets show bands of NH and of NH_2[5, 6, 8, 9] near the heads and of N_2^+ in the tails.[1–4, 7, 10]

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STARS

N_2 molecules are present in cool stars,[1, 2] but have not been observed in the solar spectrum.[3, 4]

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INTENSITIES

Two distinct problems arise in considering the intensities of molecular band-systems: (i) the relative intensity of bands within a system, (ii) the absolute intensity of the transition. Measurements of relative intensities have been made, particularly for the first positive[1, 2, 5, 10, 13] and second positive[3, 4, 5] systems of N_2. Calculations of relative intensities have been carried out for bands of the first positive[9, 12, 14] and second positive[6, 8, 12] systems and for the Vegard–Kaplan bands,[9] and for the first negative system[7, 9] of N_2^+.

A comparison of observed and calculated relative intensities for the first positive bands shows that the transition moment is not independent of internuclear distance.[10, 11]

Calculations of the absolute *f*-values for the second positive[15] and first negative[16, 17] systems have been made. In direct experimental studies, the lifetime in the state B $^2\Sigma^+$ of N_2^+ was found[18] to be $(6{\cdot}58 \pm 0{\cdot}35) \times 10^{-8}$ sec., corresponding

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to an oscillator strength for the transition B $^2\Sigma_u^+$–X $^2\Sigma_g^+$, $f=(3{\cdot}48\pm0{\cdot}20)\times10^{-2}$. Similarly the lifetime in the state C $^3\Pi_u$ of N_2 is found[18] to be $(4{\cdot}45\pm0{\cdot}20)\times10^{-8}$ sec. These figures may be contrasted with the lifetime[19] for the metastable state A $^3\Sigma_u^+$ in N_2, $t\geqslant10^{-2}$ sec.

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Active Nitrogen

When nitrogen is subjected to the action of an electric discharge, excited species are formed, and an intense afterglow may be observed following the decay of these species on switching off the discharge or on removing the gas from the discharge in a flow system. In rather pure nitrogen, the afterglow is of a striking, straw-yellow colour. This is the Lewis–Rayleigh afterglow[1–6]; the excited gas is called active nitrogen (for reviews, see[7–9]). Much work has been directed towards the elucidation of the nature of active nitrogen; the kinetics of the afterglow, the energy content of the active gas, its chemical reactions, its emission and absorption spectra and its mass spectrum, have all been studied. There is now general agreement that the active species are ^4S, ground state, nitrogen atoms.

Active nitrogen may be prepared by passing the gas through many different kinds of electrical discharges. Most convenient are tubes with external electrodes; microwave excitation may be used. It has often been stated that completely pure nitrogen does not show the afterglow,[16, 28, 31, 66] and under ordinary conditions the intensity of the afterglow generally increases for the first small amounts of added impurity. Effective impurities appear to be those which poison the walls of the containing vessel towards heterogeneous atom recombination. Indeed Rayleigh was able to prolong the life of the afterglow to more than 5½ hours in a 13-litre vessel whose walls had been treated with metaphosphoric acid (references to production and mechanism include 21, 24, 30, 38, 54, 65, 68, 70, 80, 81, 92, 93, 102–106, 110).

The spectrum[15, 23, 27, 32, 39–41, 50, 53, 57, 58, 61, 63, 69, 71–75, 77, 82, 84, 86, 87, 94, 97–99, 109] of the Lewis–Rayleigh afterglow consists largely of selected bands (particularly with $v'=12$, 11, 10 and 6) of the first positive, B $^3\Pi_g$–A $^3\Sigma_u^+$, system of N_2. In addition, quite recently, the γ bands, B^1 $^3\Sigma_u^-$–B $^3\Pi_g$, have also been identified, while observations in the Schumann region reveal emission from the Lyman–Birge–Hopfield bands, $a\ ^1\Pi_g-X^1\Sigma_g^+$. Other emission bands, $^3\Delta_u-B^3\Pi_g$ are predicted but have not yet been observed. Most probably they lie rather far in the infra-red region.

While the effect of the addition of inert gases[15, 46, 60, 72, 78, 79, 88, 90, 96, 107, 108] to active nitrogen is principally to shift the populations in the initial vibrational levels, active nitrogen reacts in a striking fashion with many substances to give quite

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new emission spectra. Thus many carbon compounds yield the spectrum of CN[13, 15, 26, 27, 76]; silicon tetrachloride affords SiN, germanium tetrachloride gives GeCl, and with oxygen[34, 35, 38, 42, 45, 47] bands of NO[22, 30, 43] are observed. Spectroscopic studies of other gas-phase reactions have been reported as follow: CO,[43] SO_2,[59] HBr, Br_2,[62] Hg,[100] metal vapours.[101, 107, 108]. Reactions with solids have also been studied.[17–20, 52, 73] These spectra are of some practical importance, in that they correspond to rotational temperatures[13, 26] (~200–300°K.) often far lower than can be obtained in other sources. Observations of this kind have been employed to assess the maximum energy that can be supplied by active nitrogen. Energies of excitation of up to 9·6 ev. have been reported,[22, 25, 30, 33, 64, 67] close to the dissociation energy of nitrogen (9·678 ev.).

Many studies of the kinetics of the afterglow have been made.[14, 29, 36, 37, 44, 47–49, 51, 55, 56, 85, 89] The intensity is found to be proportional to the square of the nitrogen atom concentration under a variety of conditions. It also varies linearly with the total pressure of nitrogen, and decreases with increasing temperature.[83, 91, 95]

The mechanism[11, 12] now established for the Lewis–Rayleigh afterglow results from the combination of direct, mass-spectroscopic, measurement of the relative concentrations of nitrogen atoms in active nitrogen with intensity measurements yielding relative molecular populations in the initial vibrational states of the afterglow spectrum.

An essential feature of the mechanism is the assumption of equilibrium between atoms and nitrogen molecules in the weakly-bound ${}^5\Sigma_g{}^+$ state. The detailed scheme is as follows:

$$\begin{aligned}
&N({}^4S) + N({}^4S) + M \rightleftharpoons N_2({}^5\Sigma_g{}^+) + M \\
&N_2({}^5\Sigma_g{}^+) + M \rightarrow N_2(B\ {}^3\Pi_g,\ v = 12, 11, 10) + M \\
&\qquad\qquad\qquad\ \rightarrow N_2(B^1\ {}^3\Sigma_u{}^-,\ v = 8, 7, 6) + M \\
&\qquad\qquad\qquad\ \rightarrow N_2({}^3\Delta_u) + M \\
&\qquad\qquad\qquad\ \rightarrow N_2(a\ {}^1\Pi_g) + M \\
&N_2(B\ {}^3\Pi_g,\ v = 12, 11, 10) \rightarrow N_2(A\ {}^3\Sigma_u{}^+,\ v = 8, 7, 6) + h\nu \\
&N_2(B^1\ {}^3\Sigma_u{}^-,\ v = 8, 7, 6) \rightarrow N_2(B\ {}^3\Pi_g,\ v = 4, 3, 2) + h\nu \\
&N_2(B\ {}^3\Pi_g,\ v = 4, 3, 2) \rightarrow N_2(A\ {}^3\Sigma_u{}^+,\ v = 2, 1, 0) + h\nu \\
&N_2({}^3\Delta_u) \rightarrow N_2(B\ {}^3\Pi_g,\ v = 7, 6, 5) + h\nu \\
&N_2(B\ {}^3\Pi_g,\ v = 7, 6, 5) \rightarrow N_2(A\ {}^3\Sigma_u{}^+,\ v = 4, 3, 2) + h\nu \\
&N_2(a\ {}^1\Pi_g) \rightarrow N_2(X\ {}^1\Sigma_g{}^+) + h\nu
\end{aligned}$$

It is an important experimental result that the vibrational levels of the states B ${}^3\Pi_g$ and B^1 ${}^3\Sigma_u{}^-$ which lie just *below* the dissociation energy of N_2 are virtually unpopulated. Studies of the variation of intensity with temperature indicate that in the limit of gas temperature, the B ${}^3\Pi_g$ molecules would be formed with an energy of about 850 cm.$^{-1}$ less than the energy of two recombining atoms. This suggests that the ${}^5\Sigma_g{}^+$ state has a dissociation energy of about 850 cm.$^{-1}$, somewhat higher than the estimates made from predissociations[10] (350 cm.$^{-1}$ from B ${}^3\Pi_g$ and 100 cm.$^{-1}$ from a ${}^1\Pi_g$).

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ABSORPTION

Active nitrogen is transparent in the visible region of the spectrum[1, 2] and earlier experiments to detect absorption in the Schumann region were unsuccessful.[3, 4] More recently the lines at 1200 A. and at 1134 A. arising from the transitions ^4P–^4S have been found to appear strongly in absorption.[5, 6] At the same time, there is observed very much weaker absorption from excited ^2D and ^2S atoms.[5] Vibrationally excited molecules ($X\,^1\Sigma_g^+$, $v=1$) have also been shown to be present; their existence had already been postulated on other grounds.[7] The presence of ground-state atoms in the afterglow was first demonstrated by the paramagnetic resonance spectrum.[8]

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PINK AFTERGLOW

Other afterglows, both of long[1] and of short[2–10] duration, may be observed in nitrogen. In particular a pink afterglow[9] which appears about 5×10^{-3} sec. after the discharge and persists for about 2×10^{-3} sec. has been studied. This short-duration glow is characterized by strong emission of N_2^+ ($B\,^2\Sigma_u^+$–$X\,^2\Sigma_g^+$) and of N_2 First

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Positive (B $^3\Pi_g$–A $^3\Sigma_u{}^+$), and of weak emission of N_2 Second Positive (C $^3\Pi_u$–B $^3\Pi_g$) bands. The glow is very readily quenched by oxygen. The existence of this afterglow shows the presence of highly energetic species other than ^{4}S nitrogen atoms after the discharge.

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Raman Spectrum

The Raman spectrum of nitrogen has been studied in some detail. The strongest line corresponds to the transition $v = 1 \leftarrow v = 0$, with $\Delta\nu = 2331$ cm.$^{-1}$. This is observed both in the liquid[1, 2] and in the gas.[3, 9] The overtone $2 \leftarrow 0$, which, for excitation by λ3650 A. is calculated to be about 490 times weaker than the $1 \leftarrow 0$ band[17], has also been observed in liquid nitrogen.[1]

The rotational Raman spectrum has been studied, particularly by Rasetti[4–8] and, with greatly improved techniques, by Stoicheff.[20, 22] The latter photographed some 35 lines of the *S* branches lying on either side of the exciting line (Hg 4358 A.). The *Q* branch of the 1–0 band appeared as a faint broad band degraded to the violet with a head corresponding to $\Delta\nu = 2329{\cdot}66$ cm.$^{-1}$ This work leads to a precise determination of the rotational constants of the $^{14}N_2$ molecule: $B_0 = 1{\cdot}9897_3 \pm 0{\cdot}0003$, $D_0 = (6{\cdot}1 \pm 0{\cdot}5) \times 10^{-6}$ cm.$^{-1}$. Combining these with values taken from the analysis of electronic bands of nitrogen, there are obtained $B_e = 1{\cdot}9987_4 \pm 0{\cdot}0003_5$ cm.$^{-1}$ and $r_e = 1{\cdot}0975_8 \pm 0{\cdot}0001$ A. The lines exhibit an alternation of intensity,[6, 16] with the lines of even *J* stronger than those of odd *J*. This proves that ^{14}N nuclei obey Einstein–Bose statistics.[8, 21]

The effect of pressure on the spectrum of the gas has been examined[10, 11] and the results of calculations and measurements of the degree of depolarization have been reported.[12–15] The ratio of the Raman intensity to the intensity of Rayleigh scattering, expressed as

$$10^3 \nu^4 I_{\text{Raman}} / (\nu - \omega_0)^4 I_{\text{Rayleigh}}$$

where ν is the incident frequency, is found[19] to be 1·6 for nitrogen. From this ratio may be determined the rate of change of polarizability with internuclear distance in the vibrating molecule.

Detailed study of the Raman effect provides information about the behaviour of the molecules in liquid nitrogen.[18] The line broadening which is observed is attributed to removal of the *m* degeneracy of the rotational energy levels in the intermolecular force fields. Removal of this degeneracy leads to a broadening of those transitions for which the transition probability depends on the anisotropic part of the rate of change of polarizability, whereas those for which *J* and *m* are unchanged and for which the transition probability depends only on the isotropic part remain unchanged.

The temperature dependence of line intensities has been studied.[23]

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Infra-red Spectra

An unperturbed homopolar molecule such as $^{14}N_2$ possesses no dipole vibration–rotation spectrum in the infra-red region. However, a very much weaker quadrupole vibration–rotation spectrum may be predicted (as has been observed for hydrogen[1]). The branches of these vibration–rotation bands would consist of O, Q and S lines. The detection of nitrogen in stellar or planetary atmospheres through these—so far unobserved—bands is possible, and the wave-lengths of some Q lines of $^{14}N_2$ have been calculated.[2] The oscillator strength of the (dipole) fundamental vibration band of $^{14}N^{15}N$ has been calculated[3] to be $f(0,1) = 2{\cdot}4 \times 10^{-14}$.

If, however, a homopolar molecule is suitably perturbed, for example by increase of pressure, or by addition of a foreign gas under pressure, a dipole vibration spectrum may be observed. Thus the fundamental bands of oxygen and of nitrogen are observed in mixtures of the gases under pressure[4] and in liquid air.[5] In pure nitrogen, the extinction coefficient of the fundamental band is proportional to the square of the density.[6] At high pressures, up to 1500 atmospheres, induced absorption in the first overtone region at 4632 cm.$^{-1}$ is also observed.[7] Likewise liquid nitrogen[8] at 69°K. shows an absorption peak at 2350 cm.$^{-1}$. These absorptions are dipole transitions induced by intermolecular forces during collisions.[4, 9, 10] Absorption[8] is also observed in solid β-nitrogen at 43·9°K. where the maximum lies at 2340 cm.$^{-1}$; the spectrum of solid α-nitrogen at 34·4°K. is more complicated, with bands at 2300, 2373 and 2400 cm.$^{-1}$

The spectrum of liquid oxygen–nitrogen mixtures also contains[11] a weak band at 10217 ± 10 cm.$^{-1}$. This is assigned to a *double* transition

$$[N_2, v = 1: O_2\ {}^1\Delta_g, v = 0] \leftarrow [N_2, v = 0: O_2\ {}^3\Sigma_g^-, v = 0]$$

for which the unperturbed energy difference would be $2330{\cdot}7 \pm 7882{\cdot}4 = 10213$ cm.$^{-1}$. Double transitions are also observed in compressed gases.[12, 13] Thus on addition of nitrogen to carbon dioxide, new bands appear at 2994 and 4670 cm.$^{-1}$. The transitions of these collision complexes are:

$$[N_2, v = 1: CO_2, 010] \leftarrow [N_2, v = 0: CO_2, 000]$$
$$2330{\cdot}7 + 667{\cdot}3 = 2998 \text{ cm.}^{-1}$$

and

$$[N_2, v = 1: CO_2, 001] \leftarrow [N_2, v = 0: CO_2, 000]$$
$$2330{\cdot}7 + 2349{\cdot}3 = 4680 \text{ cm.}^{-1}$$

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Triatomic Nitrogen, N_3

Several observations have been made which have been interpreted as indicating the existence of a triatomic nitrogen molecule. Nitrogen passed through an electric discharge and then condensed was found to show absorption[1] at 2150 cm.$^{-1}$: the absorption disappeared when the sample was allowed to warm up to 35°K. Isotopic substitution was found to split the band in a way consistent with absorption by a linear, symmetrical, N_3 molecule. Observations[2] on the photolysis of hydrazoic acid contained in a matrix suggest that N_3 is present as an intermediate, absorbing at 2140 cm.$^{-1}$ In the gas phase flash photolysis of HN_3 and of DN_3 an absorption band system at 2670 to 2730 A. is found.[3] This is in about the same place as are found characteristic absorptions of the isoelectronic species CO_2^+ and N_2O^+, and the spectrum may plausibly be attributed to a transition ${}^2\Sigma^+–{}^2\Pi_i$ in linear N_3. An observed interval of 150 cm.$^{-1}$ may then represent the ${}^2\Pi_{1/2}–{}^2\Pi_{3/2}$ separation.

A quite different kind of N_3 molecule has been suggested following measurements of the radiation emitted from solid nitrogen near 4°K. containing trapped nitrogen atoms.[4, 5] This species is thought to be weakly bound $N_2 \ldots N$. Evidence for a molecule $N_2 \ldots O$ has also been adduced from other experiments under similar conditions.

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THE SPECTROSCOPY OF CERTAIN NITROGEN COMPOUNDS

Nitric Acid

The aqueous solution of the acid has been studied in the ultra-violet region,[2, 3, 47, 49, 58, 64] and HNO_3 molecules are probably responsible for a diffuse maximum at 2600 A.; very concentrated solutions show the spectrum of the N_2O_5 molecule. The emission of ultra-violet light from the neutralization reactions of HNO_3 with NaOH and KOH has been investigated.[26, 29]

The infra-red spectra of HNO_3[54, 81] and DNO_3[81] vapours have been carefully studied, and by using Raman data for the infra-red inactive fundamentals all the nine fundamental frequencies[54, 59, 80, 81] have been assigned. The molecule can be treated as if it was partly of C_{2v} symmetry, and partly of C_s symmetry. In the pure

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liquid (studied using silver chloride windows and Teflon accessories[89]), the spectra have been shown to agree with Raman measurements, and display NO_2^+ lines at 2360 and 3745 cm.$^{-1}$.[89] Early work[1, 7, 17, 28, 34, 39, 40, 41, 51] was more concerned with finding the bands than assigning them. The infra-red spectrum has been used in analytical work to follow the concentration of HNO_3[75]; a band at 1·4 μ is used.[48, 83] The spectrum of H_3O^+ in HNO_3 has been studied.[60, 87]

The vibration frequencies[81, 89] of HNO_3 vapour are:

NO_3 part: (C_{2v}) a_1 1320, 886, 680 cm.$^{-1}$ b_2 1710, 583 b_1 765
OH part: (C_s) a' 3560, 1335 a'' 465

The Raman spectrum[70] has not been used as much to work out the parameters of the molecule as to find out what happens in mixtures of HNO_3 with water,[9, 12, 23, 35, 52, 56, 57, 79, 82, 84] sulphuric acid,[21, 25, 27, 30, 33, 53, 66, 68] sulphur trioxide,[65, 67, 76, 78, 88] acetic anhydride[24, 63, 72] and other acids; its auto-ionization in 100% solution has been studied,[70, 77] as has its dissociation.[6, 8, 15, 42, 62] The nitronium ion NO_2^+ appears whenever nitric acid is ionized,[52, 53, 56, 57, 65–71, 78, 83] and is easily recognized[53, 55, 88] by a strong line at 1400 cm.$^{-1}$. The early work on the constitution and vibrations of the molecule[4, 5, 10, 11, 13, 14, 16, 18–20, 22, 31, 32, 36–38, 43, 50, 61] has been well summarized.[70]

The microwave spectrum of nitric acid vapour has recently been analysed,[90] using the species $H^{14}NO_3$, $D^{14}NO_3$ and $H^{15}NO_3$, and the molecular geometry derived assuming the O–H bond-length to be 0·96 A.:

$r_{\text{N-OH}} = 1{\cdot}405$ A., $r_{\text{N-O}} = 1{\cdot}206$, angle O–N–O = 130°, angle N–O–H = 102°. From the Stark effect splitting the dipole moment has been calculated to be 2·16 D.; hyperfine structure quadrupole coefficients for HNO_3 and DNO_3 have also been determined. The molecule is planar, and there is a barrier to internal rotation of the OH bond of about 10 kcal./mole.

The spectra of organic compounds of nitric acid (mainly nitrates and nitro-compounds) have been investigated in the ultra-violet[73, 85, 91] and infra-red[74, 86] regions and their Raman spectra have been studied.[14, 44–46]

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Nitrate Ion

The electronic spectrum of the nitrate ion has been studied in pure molten alkali nitrates,[35, 39] and in the solids at 4°K.[36] Two transitions are found, a fairly weak $\Pi^* \leftarrow n$ transition falling between 2800 and 3100 A. (depending on the metal), and a stronger transition at 2000 A.: the latter is probably $E_1 \leftarrow A_1'$,[37] while the former[28, 36, 37, 39] might be $E' \leftarrow A_1'$[36] or much more likely,[37, 39] the forbidden transition $A_1'' \leftarrow A_1'$, borrowing intensity from the latter.[37] The orbitals involved have been discussed.[14, 32]

The 3000 A. band is diffuse in the crystal until almost liquid helium temperature[2, 3, 11, 36]; it is only seen in absorption if the light is polarized in the plane of the nitrate ions,[8, 17] and it is predissociated[1, 15, 16, 36]; this is probably photodissociation.[1, 15, 16] A lattice frequency of 70 cm.$^{-1}$ has been seen in the spectrum of solid $NaNO_3$.[19, 22]

The infra-red spectra of alkali nitrates have been observed above and below their m.p.,[38] and in an alkali halide melt.[40] The four frequencies of the ion are given,[20, 30–32, 38, 40] and the shift of ν_3 with halide used in the melt[40] has been correlated with repulsive, dipole–dipole and quadrupole–quadrupole interactions. Fine structure at 850 cm.$^{-1}$ arising from coupling of out-of-plane vibrations in KNO_3 has been seen.[34]

The interest in the Raman spectrum[23, 26, 29, 41] of the nitrate ion has mainly been directed[4–6, 7, 9, 10, 12, 13, 18, 21, 24–27] towards identifying the three allowed fundamentals in a solution of nitric acid in water; they are 720, 1050 and 1360 cm.$^{-1}$ (see also HNO_3—refs. 4, 5, 12, 32, 33). The out-of-plane vibration, active in the infra-red, is at 832 cm.$^{-1}$.

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Nitrous Acid

The study of absorption spectra, both in the infra-red[6, 9, 10–12] and in the ultra-violet,[1–5, 7, 8, 13] has been important in demonstrating the existence of the nitrous acid molecule, HONO, in the gaseous state. A system of bands in the region 3100–3900 A. is observed in absorption in NO–NO_2–H_2O mixtures at ordinary temperatures[2, 3]; similar bands appear in the products of CO–NO–H_2O explosions at high pressures.[1, 4] The identity of the emitter has been debated,[4, 5] but the isotope effect between hydrogen and deuterium[8, 13] is consistent with the assignment of the bands to nitrous acid.

Analysis of the infra-red spectrum suggests[9, 12] that the gaseous molecule may be capable of existence in two forms, perhaps *cis*- and *trans*-, of which the latter is more stable by about 500 cal./mole. Frequencies of 868 and 818 cm.$^{-1}$ in the solid state (856 and 794 cm.$^{-1}$ in the gas) seem to be associated respectively with these two forms, and these have been studied by matrix isolation methods.[15] However, the structure of the molecule does not yet appear to be known in detail. Assignments of infra-red frequencies have been made following observations both on HONO and on DONO,[12] and analogies with the spectra of alkyl nitrites[10, 11] have been helpful. Force constants have been calculated.[14]

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Nitrite Ion

The electronic spectrum[4, 5, 9, 12] consists of a weak band system at around 3500 A. (λ_{max} 3851·4 A.), a very weak system at 3100 A. and a much stronger system at 2050 A.: the polarizations,[16] electronic configurations[13–15] and symmetries[14, 15, 18] have been considered, and a vibrational analysis of the longest wave-length transition[18] for solid $^{14}NO_2^-$ and $^{15}NO_2^-$ has given the vibrational frequencies ν_1 and ν_2 for the ground and excited states. The transition is $^1B_2 \leftarrow {}^1A_1$, and the frequencies for $^{14}NO_2^-$ are $^1B_2$ $\nu_1 = 1018$, $\nu_2 = 632$ cm.$^{-1}$; $^1A_1$ $\nu_1 = 1325$, $\nu_2 = 829$ cm.$^{-1}$. The lattice frequencies were also observed.

The third fundamental has been found in the infra-red spectrum,[19] and is 1270 cm.$^{-1}$. The values of ν_1 and ν_2 derived from the electronic spectrum agree with those found in the infra-red. The infra-red spectra of aqueous solutions of simple nitrites,[7] of solid[6, 10, 11, 19] and molten[19, 21] alkali-metal nitrites, and of a single drop of nitrite solution[17] have been observed. The single-crystal values[3] for the fundamental frequencies are probably wrong.[19] The infra-red shift of nitrite ions dissolved

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in molten alkali halides has been correlated with the lattice parameters of the matrix.[20]

The Raman spectrum of the nitrite ion in aqueous solution[1–3] shows all three fundamental frequencies expected for a triangular species. The degrees of depolarization of the lines have been measured.[3] Observations on aqueous solutions of complex nitrites of platinum, palladium, rhodium and iridium have also been reported.[8]

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Organic Nitrites

The infra-red[2–8] and ultra-violet[1, 5, 7, 8] spectra of a number of alkyl and aryl nitrites have been observed.

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Nitroxyl Radical

The species HNO was first prepared[2] by the action of atomic hydrogen on nitric oxide[1]; it has also been postulated as an intermediate in several photochemical reactions. The electronic absorption spectrum was first observed in flash photolysis,[5, 6] particularly of $NO{-}NH_3$ mixtures, and also of CH_3NO_2, $C_2H_5NO_2$, and *iso*amyl nitrite. In these circumstances, the lifetime[6] of HNO is comparatively long, about 0·1 second. This spectrum has also been observed in continuous photolysis,[10] although the absorption was not strong enough to reveal the vibration–rotation spectrum. In an argon matrix[7, 9] at 4·2°K. the electronic spectrum is shifted from its position in the gas phase by 57 cm.$^{-1}$ towards longer wave-lengths.

Vibration–rotation bands ascribed to HNO have been observed in absorption,[8] (i) in the products of photolysis of methyl nitrite trapped at 20°K. in a solid argon matrix, (ii) in the products of the reaction of H or D atoms with nitric oxide, condensed on a surface cooled by liquid helium. Infra-red emission bands ascribed to this molecule have also been observed in chemiluminescence following the reaction of hydrogen atoms with nitric oxide.[11]

The positive identification of HNO and the determination of its structure follow from the detailed analysis[6] of high resolution plates of the electronic spectrum, both for HNO and DNO. This shows the structure to be HNO, and not NOH. Both ground and excited states are bent; no spin-splitting is observed in the spectrum, and it is likely that the states are singlets. This is in accord with theoretical predictions,[3, 4] which also indicate a low-lying triplet state.

	Electronic symmetry	r_{N-O}	r_{N-H}	Angle H–N–O
Upper state	$^1A''$	$1{\cdot}241_1$ A.	$1{\cdot}036_0$ A.	$108{\cdot}5_8°$
Lower state	$^1A'$	$1{\cdot}211_6$	$1{\cdot}062_8$	$116{\cdot}2_5°$

The observation of predissociations in the emission spectrum[12] leads to upper limits for the dissociation energies of 48·6 kcal. and 49·1 kcal. for HNO and DNO respectively.

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Ammonium Ion, NH_4^+

Very little work has been done in the visible and ultra-violet regions on the spectrum of the ammonium ion[44] except to show that NH_4^+ concentrations decrease in favour of NH_3,nH_2O in more concentrated aqueous solutions of ammonia,[42] and that the nitrate is covalent as vapour[26] (having a diffuse maximum at about 2620 A.). Ammonium halide–metal phosphors have been investigated.[41, 63]

In the vibration–rotation spectrum much early work was done on identifying bands in the infra-red[1–3, 16, 17, 30] and Raman[4–9, 11, 12, 14, 15, 18, 20, 21, 23, 28–31, 33] spectra, and also on showing how they behaved[34, 35] on dissolution in water[22] or other solvents.[10, 27] In general, the spectrum of NH_4^+ does not appear in solution except in strong aqueous or non-aqueous solutions of ammonium salts.[31, 34, 35] The main interest in the vibration–rotation spectrum now is to discover whether the ammonium ion is able to rotate freely in the crystal, and what happens at the phase transitions. It was found fairly soon[22, 32] that there is a change in the appearance of the spectrum at the λ-points in NH_4Cl and NH_4Br, but the interpretation is difficult,[16, 45, 52] and many speculations have been made.

Various criteria have been used[78] to decide whether the ammonium ion in a salt is freely rotating, though any one by itself is not really sufficient.[55] The criteria are:

(i) distortion of the crystal as compared to the corresponding salts of potassium and rubidium;

(ii) line width of the nuclear magnetic resonance (NMR) proton lines;

(iii) specific heat;

(iv) infra-red data, which with *X*-ray data form a fairly good test.

The NH_4^+ ion has six fundamental frequencies,[46, 70] all of which are active in the Raman spectrum, and only two of which are active in the infra-red: these latter are the N–H stretching frequency ν_3 and the NH_4 deformation frequency ν_4 (both of symmetry f_2), and they will be degenerate unless the NH_4^+ ion is unable to rotate freely, when the interaction of the symmetry of the site with that of the ion will destroy the degeneracy. This means that a molecule with blocked NH_4^+ rotation will have infra-red fundamental bands split into three components, one of symmetry type a, and two of type b; this is easily observable for ν_4, but not quite so easy to see for ν_3, since the nearby $2\nu_4$ and $\nu_4+\nu_2$ will confuse the region. There is also a correlation between the presence of a combination band $\nu_4+\nu_6$ and free rotation; those molecules in which the NH_4^+ ion is shown by NMR studies[71, 72, 73] to be not rotating have an observable $\nu_4+\nu_6$ band and, incidentally, are isomorphous with the corresponding potassium and rubidium salts.

The salts in which the ion is found to rotate include NH_4I, and others where the anion is large; the other halides, NH_4F, NH_4Cl, NH_4Br and NH_4N_3 do not have this rotation.

The spectrum of NH_4F (and ND_4F) is explained in terms of an order-disorder transition[49, 52, 55, 60, 74, 78] in a molecule of symmetry 'essentially' T_d. Its λ-point is at -30°C., this being the temperature where the higher temperature modification, in which the NH_4^+ ions are randomly positioned in their two possible orientations in the crystal (Phase II[37]), changes to another modification where the NH_4^+ ions are all parallel (Phase III). The two forms have the same overall crystalline structure, since the lattice (torsional) frequency ν_5 is unchanged at the λ-point.[59]

NH_4Cl and NH_4Br, and the corresponding deuterated molecules, are exactly similar,[55] though the λ-points are slightly lower: NT_4Cl has also been investigated.[77] In NH_4I the ion rotates about one N–H...I hydrogen bond, giving essentially C_{3v} symmetry.[74] It should be noticed that broad bands do not necessarily accompany hydrogen bonds.[57, 74]

The following ammonium salts have been studied: fluoride,[1, 32, 57, 60, 72, 74, 76, 78] chloride,[1, 3, 8, 12, 13, 15, 17, 24, 25, 28, 29, 32, 40, 45, 47–49, 52, 54, 55, 57, 59, 60, 62, 64, 67, 71, 78] bromide,[1, 25, 32, 45, 49, 50, 52, 55, 57, 60, 62, 64, 78] iodide,[1, 25, 32, 49, 57, 60, 62, 64, 65, 69, 78] sulphate,[1, 5, 6, 11, 15, 22, 33, 38, 39, 66, 67, 78] oxalate,[38] nitrate,[1, 4, 5, 7–10, 14, 15, 18, 19, 21, 27, 31, 34–36, 38, 39, 51, 53, 56, 58, 61, 67, 78] thiocyanate,[27, 78] cyanate,[78] azide,[75, 78] borofluoride,[73, 78] fluosilicate,[64] chlorostannate,[64] phosphate,[12] acetate,[38] and carbonate.[43, 67]

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Ammonia

ELECTRONIC SPECTRUM

The electronic spectrum of ammonia[1–13, 15–19, 21–25, 28–31, 33–35, 37, 38, 40–42, 44] consists of five transitions,[13, 19, 42, 44] (possibly forming two Rydberg series[42]), and ionization continua in the far ultra-violet.[29, 35] The origins of four of the transitions are at 2168, 1689, 1434, and 1330 A., while that of the fifth, which gives rise to a series of bands around 1286 A., is unknown; the transitions 2168, 1434 and 1330 A. form a progression[42]

$$\nu = 82{,}150 - R/(n - 1{\cdot}02_4)^2;\ n = 3, 4, 5$$

leading to a series limit of 10·18 e.v., in good agreement with the electron impact value of the first ionization potential, 10,154 e.v.[39]

The first four transitions almost certainly have planar upper states, while the upper state of the fifth, and the ground state of the ion NH_3^+, (of which the frequency ν_2 is 920 cm.$^{-1}$), are also probably planar.[42] The 2168 A. transition has A_2'' electronic symmetry in its upper state, and N–H bond-length greater than in the ground state: if the progression 2168, 1434, and 1330 A. is indeed a Rydberg series, it can be written as

$$(a_1')^2\,(e')^4\,(a_2'')\,(ns\,a_1')\;{}^1A_2'' \leftarrow (a_1)^2\,(e)^4\,(a_1)^2\;{}^1A_1;\ n = 3, 4, 5$$

An assignment of the vibrational structure of the 2168 A. transition, employing deuterated ammonias, has been put forward.[42]

The 1600 A. bands are sharp and perpendicular-type,[44] and the upper state has the degenerate electronic symmetry E″; possibly with the 1286 A. transition it forms a series:

$$(a_1')^2\,(e')^4\,(a_2'')\,(np)\;{}^1E'' \leftarrow (a_1)^2\,(e)^4\,(a_1)^2\;{}^1A_1;\ n = 3, 4$$

This state has been rotationally analysed, and is interesting as the first electronic transition so analysed in a symmetric-top molecule. According to the Jahn–Teller effect, the molecule in this degenerate electronic state might be unstable with respect to motions of the nuclei which correspond to the degenerate modes of vibration of the molecule, and it could then assume some symmetry lower than C_{3v}, and so split the degeneracy of the electronic state. No evidence of such an interaction has been noticed; further it should show up in the spectrum as progressions in the degenerate vibrational modes. One interesting effect is noticed, however, and that is the separation of rotational levels of symmetries A_1 and A_2 with $K = 1$ in the upper state; this, together with the surprising J-dependent separation of the $+\ell$ and $-\ell$ levels of given K, has been interpreted as a giant ℓ-type doubling (see ref. 90 of vibration–rotation spectrum), due to a strong Coriolis-type perturbation, with displacements of up to 50 cm.$^{-1}$ in the $K' = 1$ levels. This perturbation normally occurs between an A type and an E type vibrational level separated by a small energy difference, and this is unexpected for $v_2' = 1$, unless one of the degenerate frequencies, as yet unobserved, is much lower than in the ground state; hence it would be rash to rule out Jahn–Teller distortion completely.

Further into the ultra-violet[13, 16, 18, 21, 29, 35] the spectrum is continuous to at least 500 A.; the ionization potentials have been investigated and measured in various ways.[14, 20, 32, 36, 39]

The spectra of liquid[22, 28] and matrix-trapped[41, 43] ammonia have been studied, as have those of some metal ammoniates[26, 48–51]; ammonia shows a broad band at 1900 A. in aqueous solution.[7] The theory of the spectrum of metal ammoniates has

Table V.—Electronic States and Transitions in Ammonia

	T_0	ν_2	x_{22}	B_0	α_2^B	r_{N-H}(A.)	h (A.)	
E ($^1E''$)	~77000	~950					0	E ← X
D ($^1A_2''$)	75205	917	+10·0				0	D ← X
C ($^1A_2''$)	69731	911·6	+10·04				0	C ← X
B $^1E''$	59225·51	880·60	+18·437	10·29	0·577	1·027	0	B ← X
A $^1A_2''$	46136	870	+4·0				0	A ← X
X $^1A_1$	0	950·24		9·9443	0·015	1·0124	$0{\cdot}381_0$	

been discussed.[27] The electronic structure, orbitals, and possible transitions of NH_3 and NH_3^+ have been discussed[15,33,37,42] (see Table V).

An emission continuum at 5635–5670 A. is observed in discharges through streaming ammonia (Schuster's emission band).[2,45,46] In the fluorescence spectrum[47] of ammonia and excited mercury vapour, there appears a continuum from 2700 to 5600 A., with a maximum at 3400 A.

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VIBRATION–ROTATION SPECTRUM

The infra-red spectrum of ammonia[1–7] is complicated by the large number of interactions between the various energy levels, and the inversion doubling,[100] which arises as a result of the motion of the nitrogen atom through the plane of the hydrogen atoms.[25–27, 29, 30, 40, 42, 43, 45, 49–51, 55, 60, 74, 77, 96] The spectrum has been studied[9, 11, 12, 15, 18, 22] since the earliest days of infra-red spectroscopy, and a complete understanding of it has by no means been obtained, though most of the strong bands have been analysed, and many of the interactions recognized.

The effect of the inversion doubling is that ν_2, the vibration most like the inversion process, is split into two components, whose separation increases with v, being 0·66 cm.$^{-1}$ for $v_2=0$, 35·60 cm.$^{-1}$ for $v_2=1$, 284·74 cm.$^{-1}$ for $v_2=2$, and 511·34 cm.$^{-1}$ for $v_2=3$ (which lies above the hump between the potential wells of the double-well potential function). As a result, every single band in the spectrum will be doubled, by an amount depending on the values of v_2 for the transition, since infra-red selection rules only allow transitions from the lower rotational levels of one doublet vibrational state to the upper levels of another and vice versa. Even the fundamental bands ν_1, ν_3 and ν_4 are doubled, but the splitting is only about 1 cm.$^{-1}$, since $v_2=0$. As for the rotational structure, the lines will again be doubled, but they can be easily treated as if they belonged to two almost overlapping, but separate, transitions, displaced by the amount of the inversion doubling (for the statistical weights of the energy levels, see ref. 101).

Fermi resonances (between levels of the same ℓ and almost equal energy), occur very frequently in the spectrum of ammonia, for example,[92] between ν_1 and $2\nu_4^0$, and Coriolis interaction[95] between the components of a level, as between $2\nu_4^0$ and $2\nu_4^2$, causes further trouble in analysis. The influence of anharmonicity on the two degenerate vibrations[56] is responsible for the multitude of vibrational states around 10,000 cm.$^{-1}$, which have not been analysed in detail, while another complication is that Coriolis perturbations can occur between all pairs of levels except A_1 and A_1, and the effect of these can be accentuated if the levels are so close as to be in resonance; the result is a gigantic doubling[86, 90] of levels with $K=1$, and ℓ, the quantum number of degenerate vibrations, also equal to 1. This is found in ν_4, $\nu_4+\nu_2$ and $\nu_3+\nu_2$.

The regions from 500 to 7100 cm.$^{-1}$ in the spectra of NH_3 and ND_3 have been fairly extensively studied, and vibration–rotation constants of the molecules derived from careful analysis of the bands falling in them; many perturbations and interactions are described[28]. Particular attention has been paid to the bands ν_2[85, 90]; ν_4 and $2\nu_2$[90]; ν_1, ν_3 and $2\nu_4$[92]; $3\nu_2^{s,\,a}-0^{a,\,s}$, $\nu_2+\nu_4$, $\nu_3-\nu_2$ and $\nu_3+\nu_2-2\nu_2$[86]; $\nu_2+\nu_3$ and $\nu_1+\nu_2$,[88] and a good summary of the vibrational levels of NH_3 and ND_3 exists.[83] The region up to 18,000 cm.$^{-1}$ has been less thoroughly investigated.[10, 14, 16, 53, 54, 56]

The fundamental frequencies of NH_3 are:

$\nu_1(a_1)$ 3336·21 cm.$^{-1}$; $\nu_2(a_1)$ 950·24 cm.$^{-1}$ (931·66 and 964·08); $\nu_3(e)$ 3443·38 cm.$^{-1}$; $\nu_4(e)$ 1627·77 cm.$^{-1}$,

and the ground state parameters are:

NH_3 height of pyramid 0·3670 A.; r_{N-H} 1·0173 A.; angle H–N–H 107·78°
ND_3 height of pyramid 0·3687 A.; r_{N-H} 1·0155 A.; angle D–N–D 107·59°

Many theoretical treatments of the vibrations of the molecule[8, 31, 33, 34, 37, 41, 56, 57, 70, 81, 82, 84, 87, 89, 93, 94] (some including the effects of deuterium[41, 57, 62, 69] and tritium[94] substitution), of potential functions[61, 63, 64] and force constants,[65, 68, 69, 72] (see also ref. 41, p. 486), and of the magnitude of the inversion doubling[13, 17, 23, 24, 36, 47, 52, 59] have been given, while the study of line-broadening[48, 86, 92] has not been neglected.

Spectra of solid NH_3[66, 67, 91] and ND_3,[66, 67] of liquid ammonia[102, 103] and of solutions in liquid ammonia,[103] of aqueous solutions,[38, 39, 46] and metal ammoniates[76, 80] have also been taken, while the study of mixed crystals of deuterated

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ammonias[66,67,79] has enabled the fundamentals to be assigned and lattice frequencies evaluated. Crystalline hydrates of ammonia[71] have been examined and shown to be of the form NH_3,nH_2O, and the spectrum of ammonia adsorbed on catalysts[73,75,98] has been studied for a number of reasons.

The vibration frequencies of ammonia trapped in a matrix at 20°K. are little different from those in the gas phase.[97] Emission from NH_3 in ammonia–oxygen flames has been observed.[78]

Infra-red bands of ammonia reveal the presence of this gas in planetary atmospheres, particularly of Jupiter and Saturn.[104–109]

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RAMAN SPECTRUM

In the Raman spectrum of ammonia[3, 12, 13, 15, 18, 20, 23, 26, 33] the assignment of the fundamentals ν_1 and ν_3 is difficult[14, 16, 22] because the absorption is very complex[3, 13, 18] at about 3400 cm.$^{-1}$, but ν_3 has been assigned[34] in the gaseous spectrum using calculated line-intensities[19] to elucidate its fine structure. A triplet[5, 14, 16, 22, 31] at 3300 cm.$^{-1}$ has been shown to be the vibration–rotation ν_1,[31] the components being the *P*, *Q* and *R* maxima, while ν_4 has not been observed. The spectrum of ND_3 has also been investigated,[24] while force constants for NH_3[41] have been derived from the spectrum of the vapour.

Spectra have been taken of the liquid,[1, 2, 4, 10, 21, 37] the solid[36] and of various mixtures and solutions,[7, 8, 11, 21, 25, 29, 32, 38–40, 42] such as NH_3–H_2O_2,[32] NH_3–CCl_4,[38] NH_3–alcohols[39, 40] and NH_3–H_2O.[7, 8, 11, 21, 29] From the spectrum of the liquid force constants have been evaluated (the stretching constants are smaller and the bending constants greater than in the gas), while ν_3 has been seen doubled.[30] The spectra of solid NH_3 and ND_3 show ν_1, ν_2 (doubled), and ν_3, but not ν_4, and from the lattice frequencies the interaction between molecules in the crystal is calculated to be small. The spectra of the mixtures show small variations of frequency with solvent, the concentrated aqueous solution showing the spectrum of NH_3 molecules only.

Studies have been made using a circularly polarized source,[17] on depolarization theory,[27, 28] and on the polarizations of the lines themselves[6]; the effect of pressure[9, 35] on the spectrum has been investigated.

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FAR INFRA-RED SPECTRUM

The pure rotation spectrum of ammonia consists of a number of bands corresponding to the transitions $J+1 \leftarrow J$, the fine structure being due to the changes in K and the inversion doubling which doubles the levels as previously explained. The spectra of NH_3 and ND_3 have been observed in the far infra-red up to $J''=18$ for NH_3,[1–5, 8, 9, 12, 13, 15] and $J''=20$ for ND_3[4, 5, 11]; rotational constants have been determined. $J''=2-10$ has been observed for NH_2D[14, 16] and $J''=4-10$ for ND_2H.[14] The analysis of these rotational bands followed at once from application of the weight factors of the levels resulting from nuclear spin.

The inversion spectrum of the vibrational level ν_2 (which appears at about 35 cm.$^{-1}$), has been studied[16]; the transitions producing it are between the inversion-doubled levels of the state $v=1$ of the vibration ν_2.

The theory of centrifugal distortion of the levels has been considered,[7] and statistical weights of the levels have been determined.[6] The effect of pressure-broadening on the transition $J=1 \leftarrow 0$ has been studied interferometrically,[17] and the width of the line at 17·103 microns determined.[10]

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MICROWAVE SPECTRUM

The microwave spectrum of ammonia is of exceptional interest,[1, 2, 5, 7–11, 15, 20, 21, 25, 29, 33, 52, 54, 57, 68, 73, 74, 86, 87, 89, 91, 92, 97, 99, 101, 105, 111, 112] since it has some very intense lines (in fact the first lines detected in the microwave region), and it contains the transitions between the component levels of the inversion-doubled ground state. These transitions occur between those levels with the same values of J and K in the two components,[100] and give rise to lines between 7000 and 40,000 mc./sec.[10, 15, 21, 73, 91, 100, 111]; the actual inversion frequency depends on J and K as a result of the coupling of inversion and rotation, and a formula of the type[100]:

$$\nu = \nu_0 - a[J(J+1) - K^2] + bK^2 + \text{higher powers of } J \text{ and } K$$

holds. The origin of the system is at 23785·88 mc./sec.

Early workers detected that the intense lines with $K=3$ did not fit the same formula as those with $K=1,2,4\ldots$ and that they were alternately higher and lower

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in energy than expected. The reason[25,28,29] for this is that while the wave-functions for those levels where K is not a multiple of three have symmetry E, the degeneracy of which no perturbation of threefold symmetry can ever destroy, for those levels with $K=3$, each of the two sets of two levels of given J is split by a fourth order perturbation (one level of each set having symmetry A_1 and one having symmetry A_2). Now if J is odd, it is the upper level of the two that has A_2 symmetry, and if J is even, it is the lower; however since in NH_3 the A_1 levels do not occur (since the nuclear spin of hydrogen is $\frac{1}{2}$) the observed lines lie alternately above and below their unperturbed positions. For ND_3 the A_1 levels can occur, and $K=3$ is doubled, while for NHD_2 and ND_2H every line is doubled.[75] No inversion line in NH_3 can have $K=0$, because only one level exists for each J, occurring alternately in the two components of the state.

Over a hundred inversion lines have been detected in the spectra of $^{14}NH_3$ and $^{15}NH_3$,[15,21,33,50] while about thirty in the spectrum of ND_3 have been studied (the inversion frequency for ND_3 being 1591 mc./sec.)[74,86,87,112] together with the hyperfine structure of the nitrogen satellites.[112] The inversion–rotation spectra of NH_2D and ND_2H have also been studied.[68,75,76]

Early measurements of the hyperfine structure of the inversion spectrum of ammonia[5,11,13,14,16,17,19,22,26,52] were interpretable as due to the interaction between the molecular electric fields and the quadrupole moment of ^{14}N; more accurate measurements[34] indicated that small interactions between the magnetic moment of ^{14}N and a magnetic field due to molecular rotation were also present.[18,32,36] $K=1$ lines have a different hyperfine structure from the other values of K, for a doubling occurs in the quadrupole pattern increasing with increasing J due to interactions of the magnetic moments of the protons with the molecular magnetic field due to rotation, and with the magnetic moment of the ^{14}N nucleus[69,72,78,79,102]; $J=3$, $K=2$ is another case.[106] $^{15}NH_3$ does not show this as ^{15}N has no quadrupole moment. The complete structure of a line[108] then consists of a strong central main line with close magnetic satellites (caused by the reorientation of hydrogen spins[92,102]), and surrounded by an inner quadrupole doublet and outer quadrupole multiplet. The nuclear quadrupole resonance spectrum of NH_3 has been studied.[110]

Studies of the Zeemann effect give the rotational magnetic moment of the molecule and the molecular g-factor[6,43,65,103]; this can be done on the inversion spectrum where $\Delta J=0$ (it is noteworthy that the rotation spectrum selection rule $\Delta J=\pm 1$ gives gives rise to an anomalous Zeemann effect). The g-factors for ^{14}N and ^{15}N have been given as 0·484 and 0·477 nuclear magnetons per rotational quantum number.[42,57,66,80,83]

The theory[3,39,41,44,48,61,62] of pressure-broadening[12,24,38,53,55,59,60,63,67,70,82,84] of the microwave lines has been considered, and quantitative calculations enable line-broadening collision cross-sections of the ammonia molecule to be worked out from known intermolecular interactions. Collision cross-sections[44,64,71,90] for other molecules can be calculated from line-broadening measurements, by considering the interaction of the quadrupole moment of ammonia and the dipole induced in the foreign gas; such measurements have suggested a permanent quadrupole moment for N_2.

The inversion frequency of ammonia is also known to vary with pressure,[37,39,47,49,56,58,85,88,107] the theory stating that the second-order non-adiabatic effect of the electric dipole–dipole interaction between two (or possibly more) ammonia molecules[46,109] causes the doublet levels to change their spacing in a way which produces two possible transitions at different frequencies, one larger than the normal value and one smaller, the smaller gaining in intensity at the expense of the larger. There was doubt concerning the theory, but the facts are that for NH_3 the inversion frequency drops to zero at a pressure of about two atmospheres,[37] while for ND_3[85] the same drop occurs at about 9 cm. pressure. It should be noted that the ratio of these pressures is about 15:1, the same as the ratio of the inversion frequencies.

A saturation effect for microwave absorption occurs[12,16,23,25,31,35,40]; at high energies transitions are induced at a rate comparable to the collision rate, thus

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invalidating the assumption of thermal equilibrium in the line-broadening equations. Increase of power broadens the line, decreases the peak absorption coefficient, and the power absorbed approaches saturation. The saturation effect varies directly with the power and as the inverse square of the line-width; collision cross-sections can again be worked out.

Studies of the Paschen–Back effect[51] in ammonia have been made, and values for the dipole moment[45, 77] (1·468 *D*) have been obtained from the Stark effect.[6, 27, 76, 77, 81] The very accurately measured inversion lines of ammonia have prompted speculation concerning the possibilities of using them as frequency standards for an atomic clock.[4, 30, 96, 104] The temperature dependence[93–95] of the absorption coefficient is approximately $\alpha T^{-3} = \text{constant}$.

The minimum detectable absorption[113] and the application to isotopic analysis[114] have been considered.

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The NH_2 Radical

Bands of the radical NH_2 can be observed in emission in discharges in ammonia,[1, 4, 6, 14, 22, 23, 27, 29, 41, 45] by photo-dissociation of ammonia and hydrazine,[8] in the explosive decomposition of hydrazoic acid,[15, 25] and in flames of N_2O–H_2,[5, 9] N_2H_4–O_2,[30, 31] and ammonia with O_2,[2–4, 11, 17] F_2,[12] ClF_3,[28] NO_2[26] and HNO_3[26]; a high-voltage arc[13] will also give NH_2 bands. In absorption the bands can be obtained by the flash photolysis of ammonia,[16, 18, 34, 40] hydrazine[19, 36] or hydrazoic acid[32]; continuous photolysis does not appear to work well.[20, 42]

The bands that have been most widely studied are the so-called α-bands of ammonia, which lie between 3900 A. and 8300 A., and which were first found by passing discharges through ammonia. These have been most carefully analysed in absorption,[33, 34, 40] using $^{14}NH_3$, $^{15}NH_3$ and $^{14}ND_3$ in flash photolysis experiments, and the spectra of NH_2 and ND_2 are found[40] to consist of a long progression of Type *C* bands (for which the transition moment is perpendicular to the plane of the molecule), together with part of a subsidiary progression. The main progression is $(0, v_2', 0) \leftarrow (0, 0, 0)$ with $v_2' = 3, 4 \ldots, 18$,[40] and the subsidiary is $(1, v_2', 0) \leftarrow (0, 0, 0)$, deriving its intensity from Fermi-type resonances between the levels $(0, v_2', 0)$ and $(1, v_2'-4, 0)$, with matrix elements W_{ni} about 68·3 cm.⁻¹. Rotational analyses of these have given the ground state dimensions of the molecule: $r_{N-H} = 1{\cdot}024 \pm 0{\cdot}005$ A.; $H\text{–}\hat{N}\text{–}H = 103° 20' \pm 30'$.

The upper electronic state of these bands is linear, and the very complex vibronic structure of the transition has been shown to be the result of the splitting of the upper electronic Π state by electronic-vibrational coupling (Renner Effect).[7, 35, 39, 40, 43] This effect occurs (when the energy conditions[40] are suitable) in linear molecules in which the electronic orbital angular momentum Λ couples with I, the angular momentum associated with the bending vibration, to produce a resultant $K = |I \pm \Lambda|$ which is then the only 'good' quantum number. The effect then takes the form of a repulsion between levels of the same value of K, possibly amounting to several hundred wave-numbers and, for an electronic Π state, divides it into two parts: in the upper part the successive levels of the bending vibration then consist alternately of Σ, Δ, Γ, ... and Π, Φ, ... vibronic sub-levels, each set roughly obeying the formula $\nu_0^{k'} = \nu_0 - GK'^2$, with G about 28 cm.⁻¹ in the case of NH_2 and 19 cm.⁻¹ for ND_2 (which is not unlike a Σ state with huge anharmonicity). An unsuccessful search was made for H and I vibronic sub-levels.

The rotational structure of the bands resulting when these levels combine with the bent ground state levels is complicated by the spin-splitting and the K-type doubling of the upper Π state, which varied from sub-level to sub-level, being both large in the Π sub-levels, but not so significant in the Δ, Φ and Γ states; in the analysis no satisfactory formulae for the rotational term values of the Π, Δ, Φ and Γ sub-levels could be found. The bond length derived was $r_{NH} = 0{\cdot}976$ A.

The transition giving rise to the bands is:

$$K\,(a_1)^2\,(b_2)^2\,(a_1)\,(b_1)^2\ {}^2A_1 \leftarrow (a_1)^2\,(b_2)^2\,(a_1)^2\,(b_1)\ {}^2B_1$$

though to be strict the upper state, which is 'half a Π state', should be called $^2A_1\Pi_u$; both states correlate with the lowest $^2\Pi_u$ state of the linear configuration.[21]

At liquid helium temperatures[24, 37, 38, 42] the trapped NH_2 molecule shows a shift of 25 cm.⁻¹ from the vapour, and the variability of the shift indicates the presence of perturbations on the vibrational levels; the bands of the main progression could be followed up to $v_2'=22$.

The presence of NH_2 in cometary spectra is discussed.[10, 44]

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Hydroxylamine

The infra-red spectrum of hydroxylamine, as vapour,[3] liquid[3] and as solid[4] has been observed, as has the spectrum of solid ND_2OD,[4] and a fairly complete assignment of the vibrational structure has been made. Eight of the nine fundamentals are immediately obvious, and a rotational analysis of one of them has given the molecular dimensions: the molecule is a near-symmetric top of symmetry C_s.

$$r_{\text{N–O}} = 1{\cdot}46\ \text{A.}; \qquad r_{\text{O–H}} = 0{\cdot}96\ \text{A.}; \qquad r_{\text{N–H}} = 1{\cdot}01\ \text{A.}$$

$$\text{angle H–O–N} = 103^\circ; \qquad \text{angle H–N–O} = 105^\circ; \qquad \text{angle H–N–H} = 107^\circ$$

In the vapour and liquid, at least two of the bands are double, possibly owing to the existence of *cis*- and *trans*- forms of the molecule; this is particularly marked in the

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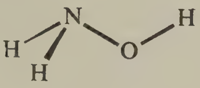
band at 1115 cm.$^{-1}$ (ν_s, a'). In the solid two types of bands appear, depending on whether the films observed are deposited at −78°C. or −190°C.; the lower temperature film gives broad overlapping bands in its spectrum, while at −78°C. the film shows narrow bands (some of which are split) of the stable crystalline form. The displacement of the OH stretching frequency to 2867 cm.$^{-1}$ probably indicates strong hydrogen bonding in the solid.

The molecule has the structure



and is definitely not $NH_3 \rightarrow O$.

The Raman spectrum has been observed[1, 2] and assigned.[3] No attempt seems to have been made to observe the inversion spectrum in the microwave region.

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HYDROXYLAMMONIUM HALIDES

Infra-red spectra of sublimed films of hydroxylammonium chloride, bromide and iodide have been obtained at several temperatures, both for the normal and deuterium-substituted compounds,[8] while spectra of the chloride in a nujol mull[4, 7] and in pressed KBr[1] have also been observed. The region from 400 to 4000 cm.$^{-1}$ has been studied, and the bands vibrationally assigned,[8] considering the molecule as part C_{3v} (H_3NO) and part C_s (OH) symmetry; the nine fundamentals can then be described as a' OH bend and stretch; a'' OH twist; a_1 NH_3 stretch and deformation and NO stretch; e NH_3 stretch, deformation and rock.

The Raman spectra of the solid[5] and aqueous solutions[2, 3, 6] of the chloride have been observed and assigned.[8]

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The NH Radical

The NH radical can be prepared in a number of ways. Its electronic emission spectrum can be excited (i) by the action of excited mercury atoms on a nitrogen–hydrogen mixture,[5] (ii) by a discharge[10, 11, 29, 41] or high-voltage arc[23] through the same mixture, (iii) by the action of atomic hydrogen on hydrazoic acid,[27, 34, 38, 41, 43, 44, 46] (iv) by a discharge through ammonia,[6, 8–10, 12, 13, 16, 17, 22, 28, 32] and (v) in many assorted flames of nitrogen compounds.[1–4, 7, 19–21, 24, 25, 29, 33, 37, 48] In absorption the radical can be produced and observed (i) in the thermal decomposition of ammonia[14, 15] and (ii) in the flash photolysis of ammonia,[36] cyanic acid,[45] hydrazine[31] or hydrazoic acid.[30, 35] ND spectra can be observed starting with deuterated materials in exactly the same ways.

The radical is possibly responsible for a band at 10,000 A. in the spectrum of the night sky,[26] and its presence in cometary spectra is discussed.[18] The spectrum of the radical trapped at liquid helium temperature in a solid matrix has been recorded.[39, 42]

Six electronic states are known,[49] four of which are singlets and two triplets: the states $c^1\Pi$, $A^3\Pi$ and $a^1\Delta$ correlate with the excited products $H(^2S)+N(^2D)$ while $X^3\Sigma^-$ correlates with $H(^2S)+N(^4S)$: the $^1\Sigma^+$ states form a Rydberg series.

The multiplet splittings in the $A^3\Pi$ state are anomalous and are interpreted[50] in terms of a perturbation with the $c^1\Pi$ state.

The dissociation energy is not known precisely; the best present estimate[27] seems to be 3·8 ev. or 88 kcal. mole^{-1}.

Table VI.—Electronic States in the Radicals NH *and* ND

NH	T_e	ω_e	$x_e\omega_e$	B_e	α_e	r_e	Refs.
$d^1\Sigma^+$	a+70539	2640		14·085*		1·128*	6, 16
$c^1\Pi$	a+30755·5*	2502	190	14·81	1·38	1·103	6, 9, 10, 12, 13, 16, 32, 43
$A^3\Pi_i$ (A = −34·7)	29776·8	3188	87·5	16·3221*	0·744*	1·037	14, 27, 34, 38, 41, 44–47
$b^1\Sigma^+$	a+8540	3480		16·401*		1·045*	13, 32
$a^1\Delta$	a(~5600)	3314	63	16·78	0·67	1·034	9, 10, 12, 32, 43
$X^3\Sigma^-$	0	3266	78·5	16·3454*	0·646*	1·038	14, 27, 34, 38, 41, 44–47
ND							
$d^1\Sigma^+$							
$c^1\Pi$	a+30848*	1828	101	7·89	0·52		10
$A^3\Pi_i$	29809	2338	49	8·73			43, 44, 46
$b^1\Sigma^+$	a+8500†						32
$a^1\Delta$	a(~5600)	2421	34	8·96	0·24		10
$X^3\Sigma^-$	0	2424	50	8·76			43, 44, 46

* Values of T_{00}, B_0, α_{10}, r_0, rather than equilibrium values.

† Approximately.

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The NH$^+$ Molecule Ion

Bands of the NH$^+$ molecule-ion may be excited in hollow-cathode discharge tubes in flowing ammonia.[1, 2] The rotational analysis of two bands has been performed,[2] and shows that the bands arise from a transition $^2\Sigma^+$–$^2\Pi_r$. The lower state, $^2\Pi_r$, is strongly perturbed by a $^4\Sigma^-$ state, and it has not yet been decided which of these interacting states is in fact the ground state. The $^4\Sigma^-$ state, though correlating with the lowest states of the separated atoms, N(^4S_u)+H$^+$(^1S_g), represents an excited electron configuration $K(2s\sigma)^2\,(2p\sigma)\,(2p\pi)^2$, whereas the $^2\Pi_r$ state arises from the lowest electron configuration $K(2s\sigma)^2\,(2p\sigma)^2\,(2p\pi)$, but correlates with excited products, N$^+$(^{3}P$_u$)+H(^2S_g), on dissociation. The constants for the states are as follows:

State	T$_{00}$	ω_e	$x_e\omega_e$	B_e	α	10^4D	r (A.)
$^2\Sigma^+$	$a+34553{\cdot}0$	2310	153	13·231	0·766	19·2	1·164
$^2\Pi_r$ (A=8·5)	a	$\Delta G_{1/2}=2755$		$B_o=15{\cdot}252$		14·3	1·084
$^4\Sigma^-$	0			$B_v=14{\cdot}94$			$r_v=1{\cdot}095$

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N—H, N—C and N—O Vibration Frequencies

N–H, N–C and N–O vibration frequencies in a wide range of polyatomic molecules have been studied. References are as follows:

N–H (infra-red): 1–8, 20, 21, 23–25, 27, 29, 32, 33, 36–38
N–H (Raman): 9, 13–16, 20, 28, 30, 39
N–C (infra-red): 22
N–C (Raman): 10–12, 15, 17–19, 26
N–O: 34, 35

Force-constants in N–H bonds have been discussed,[31] and the structure of the 10μ band of methylamine has been resolved.[23]

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Hydrazine

The electronic spectrum of hydrazine[4] shows a series of bands at 2500–2280 A., and a continuum from 2000 to 1300 A.; the N–N bond probably breaks[4] at 2270 A. (122·4 kcal./mole).

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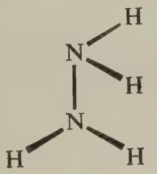
In the infra-red[7, 9, 10, 14, 15] and Raman[1, 2, 8, 9, 11, 13, 20] spectra twelve fundamentals should appear, and the complex spectra after considerable argument have been assigned[15] in terms of eleven of these; the difficulty was that the torsional vibration ν_7, though permitted by the infra-red selection rules, could not be found, although its position was suspected[13] from the presence of various difference bands in the Raman spectrum. Its discovery in the far infra-red at 376·74 cm.$^{-1}$ together with an overtone (665·9 cm.$^{-1}$) and a 'hot' band (289·5 cm.$^{-1}$) has been announced recently, and followed up with a rotational analysis.[18]

Rotational analyses have also been given[15] for the strong bands at 950 cm.$^{-1}$ (ν_{12}, *b*), 1098 cm.$^{-1}$ (ν_4, *a*) and 1275 cm.$^{-1}$ (ν_{11}, *b*), and the constants derived[15, 18] indicate:

$$r_{\text{N–N}} = 1{\cdot}453 \pm 0{\cdot}005\ \text{A.}; \qquad r_{\text{N–H}}\ \text{between}\ 1{\cdot}020\ \text{and}\ 1{\cdot}025\ \text{A.};$$
$$\text{angle N–N–H between } 112^\circ \text{ and } 112^\circ\ 30'$$

The five structural parameters required for a complete determination of the structure cannot be ascertained without the use of isotopic substitution, but the present view is that the configuration of the molecule is right-angled[3, 14, 18]:



The N–H distance found is larger than that in ammonia (1·017 A.) but is in agreement with electron diffraction results.[19]

As would be expected by analogy with ammonia, there is inversion doubling[13, 15] in the NH_2 wagging vibrations, which doubles the bands at 833 and 950 cm.$^{-1}$ exactly as in ammonia; the magnitude of the doubling, 35 cm.$^{-1}$, is also similar.

In the microwave region,[16] two hundred lines have been seen but not analysed; the structure of the spectrum is very complicated as a result of the inversion of each NH_2 group and inversion–internal rotation interaction. Some Stark effect splitting has been observed, and also some hyperfine structure due to the quadruple coupling of the two nitrogen nuclei with the overall and internal rotations of the molecule.

Hydrazine flames have been studied in emission in the infra-red,[17] and photodissociation[6] of the molecule has been investigated. The Schuster bands of ammonia have been assigned to hydrazine[5, 12] (and to NH_3).

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HYDRAZINIUM IONS

The infra-red[3, 4] spectra of $N_2H_5^+$ and $N_2D_5^+$ in the hydrazinium chlorides and bromides have been studied, and the exceptionally broad regions of absorption corresponding to the N–H and N–D stretching frequencies have been considered in terms of possible hydrogen bonding.

The Raman spectra[1, 2] of $N_2H_5^+$ and $N_2H_6^{++}$ have been investigated in aqueous solution; powdered crystals have also been examined.[5]

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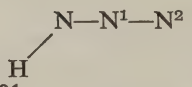
Hydrazoic Acid

The vibration–rotation spectrum[1–6] of the non-linear, planar molecule HN_3 stretches into the photographic infra-red region, and quite a detailed analysis[4, 6] of a band at 1·047 μ (observed with a path of 400 cm. at about 0·5 atm. pressure) has been given. The microwave spectrum has also been studied[8, 9] and leads to the following structure:



$$r_{\text{N–H}} = 1{\cdot}021 \pm 0{\cdot}01\ \text{A.};\qquad r_{\text{N–N}^1} = 1{\cdot}240 \pm 0{\cdot}003\ \text{A.};$$
$$r_{\text{N}^1\text{–N}^2} = 1{\cdot}134 \pm 0{\cdot}003\ \text{A.};\qquad \text{angle H–N–N}^1 = 112.65^\circ \pm 0.5^\circ;$$
$$\text{angle N–N}^1\text{–N}^2 = 180^\circ$$

The Raman spectrum has also been examined,[7] and the photolysis of the molecule has been followed spectroscopically.[10] The vibration frequencies of the molecule trapped in a matrix at 20°K. are little different from those in the gas phase.[11]

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AZIDES

The Raman spectrum of the azide ion in aqueous solution[1] shows one strong line, $\nu_1 = 1348$ cm.$^{-1}$, and a much weaker shift at 1258 cm.$^{-1}$, interpreted as $2\nu_2$. That only one fundamental is observed indicates that the ion is linear and symmetric.[1, 2] The Raman[3, 4] and infra-red[5] spectra of a number of crystalline azides have also been investigated.

Absorption of the ion in solution becomes measurable at $\lambda < 2750$ A.; this absorption[6] is attributed to a charge-transfer process:

$$N_3^-,H_2O + h\nu \rightarrow N_3,H_2O^-$$

The Raman spectra of a number of organic azides have been studied.[7]

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Nitrous Oxide

ULTRA-VIOLET SPECTRUM

The electronic spectrum of nitrous oxide begins at about 2100 A., and consists of a number of diffuse bands,[1, 2, 4–8, 11, 13, 18] 2100–1600 A. (the *B* bands[13, 19]), 1550–1400 A. (showing a possible vibrational interval of 621 cm.$^{-1}$), 1190–1130 A. (which have been assigned to three progressions, with vibrational intervals 1328, 1518 and 816 cm.$^{-1}$) and 890–860 A. Studies have been made mainly with regard to the effects of pressure[12] and temperature[13–17, 19] on the absorption, though some interest has been shown in the dissociation products of the molecule.[3, 20] Strong isolated continuous absorption[24] occurs at 1284 and 1096 A.

There are also several Rydberg series,[1, 9, 22–24] the two lowest being given by:

$$\nu = 104{,}000 - R/(n+0{\cdot}40)^2; \qquad n = 2, 3, 4\ldots$$
$$\nu = 104{,}300 - R/(n+0{\cdot}32)^2; \qquad n = 2, 3, 4\ldots$$

and corresponding to ionization potentials of 12·89 and 12·93 e.v. respectively. (This is in agreement with the photo-ionization value for the 1st I.P., 12·90 ± 0·01 e.v.) The separation of about 300 cm.$^{-1}$ corresponds to the splitting in the $^2\Pi$ ground state of the N_2O^+ ion. Another series converges to a limit at 16·39 e.v.; associated with it is an interval of 1280 cm.$^{-1}$, possibly ν_1 of the excited state B $^2\Sigma^+$ of the ion N_2O^+. An ionization potential of 16·55 e.v. has been suggested, while four series converge to a third I.P. at 20·10 e.v.

Further into the ultra-violet[10, 21] are band systems at 375,000–200,000 cm.$^{-1}$ and 600,000–400,000 cm.$^{-1}$ (weak).

Possible transitions have been considered.[16]

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INFRA-RED SPECTRUM

The infra-red spectrum of N_2O[1–7, 9–11, 16, 19, 21–23, 26, 27, 29, 30, 37, 39–43, 46–52, 56, 58–60] has been extremely carefully observed, and a total of ninety vibrational levels has been found; the spectrum has been studied up to 14,000 cm.$^{-1}$, and particular care has been given to the regions 500–5500 cm.$^{-1}$[60] and 8000–14,000 cm.$^{-1}$.[23] Several workers have used ^{15}N-substituted molecules.[21, 22, 43, 45, 56]

A complete list of vibrational frequencies, zero-order vibrational frequencies, rotational constants, force constants, anharmonicity constants, *l*-type doubling constants[43] and variation of centrifugal distortion constants with v and l[51] exists[60]; some Fermi interactions and rotational perturbations have also been studied. The vibration frequencies[60] are given as:

$$\nu_1:\quad 1276{\cdot}522\ \text{cm.}^{-1}$$

$$\nu_2:\quad 589{\cdot}193$$

$$\nu_3:\quad 2222{\cdot}745$$

while the rotational constants are $B_0 = 0{\cdot}4190153$; $D_0 = 1{\cdot}7879 \times 10^{-7}$ cm.$^{-1}$. Earlier constants[43] gave bond distances:

$$r_{\text{N–N}} = 1{\cdot}1257 \pm 0{\cdot}0020\ \text{A.}; \qquad r_{\text{N–O}} = 1{\cdot}863 \pm 0{\cdot}0020\ \text{A.}$$

The molecule is linear.

Many atmospheric bands in the solar spectrum have been investigated,[8, 15, 17, 18, 20, 24, 25, 28, 33–36] and from some of them the concentration of N_2O in the atmosphere has been estimated.[14, 38, 57] Pressure modulation studies[54, 55] have been carried out on some of the bands of N_2O with a view to observing lines of higher J, and studies have also been made of line breadths,[12, 13] torsional frequencies,[58] intensities of IR bands,[31, 32] the solid state,[53] and some theoretical aspects.[44, 61, 62] The spectra of flames supported by nitrous oxide have been examined.[63, 64]

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RAMAN SPECTRUM

Several studies of the Raman spectrum of nitrous oxide have been made. The vibrational spectrum of the gas[1, 2, 4–6] consists of two strong lines at $\Delta\nu = 1285$ and $2223{\cdot}5$ cm.$^{-1}$. These shifts agree in position with the origins of observed infra-red bands and represent fundamental frequencies ν_1 and ν_3 respectively.[3] The existence of two Raman-active fundamentals shows that the N_2O molecule cannot have a centre of symmetry. A number of weaker lines have also been observed and analysed.[7] The Raman spectrum of the liquid has also been examined,[4] and differences between the gas and liquid spectra considered.[10] Unsuccessful attempts to resolve the rotational spectrum have been reported.[8, 9] Degrees of depolarization in the Raman spectrum have been discussed[11] and measurements on the gaseous oxide have been made.[12]

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PURE ROTATION SPECTRUM

In the microwave region,[1–10] the transitions $J = 0 \rightarrow 1$ and $1 \rightarrow 2$ have been observed,[1, 10] and nuclear quadrupole coupling constants derived from the Stark effect.[1, 3, 10] The microwave Zeemann splitting[4, 7] of rotational lines has also been used to evaluate the rotational g factor. The dipole moment[5, 6] has been calculated, and, using $^{13}N_2$, centrifugal distortion constants[8] and rotational constants have been evaluated.

In the millimetre wave[11] region, the pure rotational transitions from $J = 3 \rightarrow 4$ (at $\lambda = 3$ mm.) to $J = 11 \rightarrow 12$ (at $\lambda = 1$ mm.) have been observed, and the l-type doubling constant evaluated:

$$q = \frac{\Delta\nu}{2(J+1)} = 23{\cdot}736 \text{ Mc.} = 79{\cdot}18 \times 10^{-5} \text{ cm.}^{-1}$$

The planet Jupiter,[12] unlike the Earth, Mars and Venus, shows considerable microwave absorption due to N_2O.

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The Gaseous Ion, N_2O^+

One ultra-violet band system of the gaseous ion N_2O^+ is known.[1,2,4] The rotational analysis of the (0, 0) band at 3541 A. shows that the ion is linear in both ground and excited states, and that the transition is $B^2\Sigma^+$–$X\ ^2\Pi_i$. Similar transitions are known in CO_2^+ and CS_2^+. The electronic energy, 3·492 e.v., agrees well with the difference of two of the Rydberg series limits of N_2O.[5]

The mean life-time of the upper state, $B^2\Sigma^+$, is found[3] to be $(2{\cdot}6 \pm 0{\cdot}2) \times 10^{-7}$ sec., corresponding to an oscillator strength $f = (3{\cdot}65 \pm 0{\cdot}28) \times 10^{-3}$.

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Nitric Oxide

Electronic band-systems of the nitric oxide molecule may be observed quite readily, both in absorption[5–10] and in emission, and their study has played an important part in the development of band spectroscopy.[3,11,12,17] Sources of the emission bands include:

uncondensed[1,2,18,19] and condensed[4] discharges,
high-frequency discharges,[22,23,26,27,30]
glow discharges,[24,34,35]
sparks,[29]
afterglows,[16,25]
active nitrogen,[13,18,28]
and flames.[31,32]

Bands have also been observed in the auroral spectrum,[33] and in fluorescence from nitrous oxide.[20]

Qualitative studies of the Zeeman effect have been made[14,15]; no Stark splitting was observed.[21]

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ELECTRONIC SPECTRUM

Several electronic states for nitric oxide have been found, belonging mainly to a doublet system, and all the strong transitions found lie far in the ultra-violet[19]. The forbidden transition $a^4\Pi$–X $^2\Pi$ (the *M* bands) has been studied, and a quartet–quartet transition, $b^4\Sigma$–a $^4\Pi$ is suspected also.[54, 55] Various Rydberg series are found in the ultra-violet region[35]; states $A^2\Sigma$, $E^2\Sigma$ and $P^2\Sigma$ converge to a limit, while states D and M possibly form part of a series converging to the same limit. All the absorption bands of wave-length longer than 1600 A. have been assigned.[66] Further in the ultra-violet[64, 76] a discontinuity exists at 170,000 cm.$^{-1}$ (21·2 e.v.) which is ascribed to ionization.

Fairly clear evidence of dimerization[17, 40–42, 45, 47] into N_2O_2 molecules has been put forward from observations of a broad diffuse band at 2100 A., showing a possible vibrational interval of 140 cm.$^{-1}$, which can be compared with a Raman frequency[41] of 167 cm.$^{-1}$.

The effect of temperature on the absorption has been studied.[76]

Table VII.—Electronic States and Constants of the Molecule $^{14}N^{16}O$

State	A	T_0	ω_e	$x_e\omega_e$	B_e	$10^2\alpha_e$	r_e
$P^2\Sigma$		66973·1			1·994*		1·064*
$M^2\Sigma$		64660·0			2·010*		1·060*
$I^2\Pi$		63826·4			1·43*		1·26*
$F^2\Sigma$		62039·6			1·964*		1·072*
$E^2\Sigma^+$		60862·8	2373·66	15·87	$1{\cdot}986_3$	1·82	1·0660
$B'^2\Delta_i$	−2·4	60019·1	1216·6	15·88	1·330	1·9	1·303
$D^2\Sigma^+$		53291·2	2323·9	22·89	2·0026	$2{\cdot}17_5$	1·0617
$C^2\Pi$	small + ve	52376	2395	15	2·002	3·0	1·062
$B^2\Pi_r$	30	45485·7	$\begin{cases}1038{\cdot}41\\1036{\cdot}96\end{cases}$	7·6	1·177 1·076	1·89 1·16	1·385 1·448
$A^2\Sigma^+$		44199·2	2374·8	16·46	$1{\cdot}997_2$	$1{\cdot}92_8$	1·0632
$a^4\Pi$							
$X^2\Pi_r$	124·2	0	$\begin{cases}1903{\cdot}68\\1904{\cdot}03\end{cases}$	13·97	1·7046	1·78	1·1508

The values of T_0 give the heights of the lowest levels with respect to $^2\Pi_{1/2}$, $J=\frac{1}{2}$, in $X^2\Pi_r$; they therefore correspond to the wave-numbers of the $Q_{11}(\frac{1}{2})$ lines of the transitions to X. except for *B′*, where T_0 indicates the value of $J=2\frac{1}{2}$ in $^2\Delta_{5/2}$ above $X^2\Pi_{1/2}$, $J=\frac{1}{2}$.

* Values of B_0 or of r_0.

Table VIII.—Band Systems of the Molecule $^{14}N^{16}O$

Transition	Absorption or emission	Remarks	References
$a^4\Pi - X^2\Pi$	*e*	M bands	28, 84
$b^4\Sigma - a^4\Pi$	*e*	analysis incomplete	34, 53–55
$A^2\Sigma^+ - X^2\Pi$	*a, e*	γ bands	1, 4, 6, 7, 9, 10, 12, 23, 24, 26, 29, 33, 61, 66, 68, 73, 75
$B^2\Pi - X^2\Pi$	*a, e*	β bands	1–3, 5, 7, 10, 30, 31, 33, 49, 61, 67, 68, 70, 72, 81
$C^2\Pi - X^2\Pi$	*a, e*	δ bands	1, 2, 5, 8, 13, 25, 27, 31, 33, 48, 49, 61, 70, 72
$D^2\Sigma^+ - X^2\Pi$	*a, e*	ϵ bands	18, 20, 21, 24, 26, 33, 44, 56, 66, 68,
$D^2\Sigma^+ - A^2\Sigma^+$	*e*		34
$B'^2\Delta - X^2\Pi$	*a, e*	β' bands	37–39, 46, 49, 50, 57, 62, 63
$B'^2\Delta - B^2\Pi$	*e*		32, 37, 51, 63
$E^2\Sigma^+ - X^2\Pi$	*a*		36
$E^2\Sigma^+ - A^2\Sigma^+$	*e*		14–16, 22, 34

The electronic structures of the ground[11, 36, 62, 80, 83] and excited[11, 62, 80] states have been considered, and calculations made of the first ionization potential[80] and of the magnetic hyperfine structure constants.[83] A quartet state, $^4\Pi$, is predicted[80] to lie 3·9 e.v. above the ground state X $^2\Pi$.

The first ionization potential of NO is $9{\cdot}25 \pm 0{\cdot}02$ e.v.; this value has been determined both by photoionization,[52, 69] and by electron-impact[43, 58, 78] studies.

Absolute integrated intensities of nitric oxide bands[59, 71, 79, 85] of the β, γ, δ and ϵ systems have been measured; for the β-system, $f = 0{\cdot}00151 \pm 0{\cdot}00011$, and for the γ system $f = 0{\cdot}00240 \pm 0{\cdot}00012$. Vibrational transition probabilities in the β-bands have been calculated[60, 72, 74, 77, 82] and some Franck–Condon factors considered.[60, 70]

For other intensity measurements, particularly on lines and bands of the γ system, see references 32, 87–93.

The emission of the β-bands of NO, B $^2\Pi$–X $^2\Pi$, has been observed from the solid products from gas discharges trapped at liquid helium temperatures.[65, 84] There are only small changes of the molecular constants when the molecule is trapped in the solid, as compared with the free gaseous molecule.

The effects of argon and of nitrogen at pressures up to 1000 atm. on the ultraviolet absorption spectrum have been studied[86] and indicate association between NO and N_2.

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DISSOCIATION ENERGY

Several different values for the dissociation energy of nitric oxide have at one time or another been advanced[1–17] (see also refs. 3, 18, 20, 24–27, 29 above), by methods which have included the extrapolation of vibrational energy levels, interpretation of predissociations, and electron impact studies. D_0''(NO) is of course linked with the dissociation energies of N_2 and of O_2, which are now established. The value for D_0''(NO) is 6·49 e.v. or 150·0 kcal. mole^{-1}.

One feature of the NO spectrum is of especial interest in connexion with the determination of dissociation energies: this is the interaction between the states $B^2\Pi$ and $C^2\Pi$, whose potential curves are found, experimentally, to cross (refs. 61, 72 above).

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ASTROPHYSICAL SIGNIFICANCE

Nitric oxide is of some astrophysical importance, and emission of some of its bands appears to contribute to the light of the night sky.[1–4] Photo-ionization[5, 6] in the upper atmosphere is discussed, and ionization by election impact[7] has been examined.

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INFRA-RED SPECTRUM

A number of studies of the absorption spectrum of gaseous nitric oxide in the infra-red region have been made. The structure of the fundamental, 1–0, band has been investigated[1, 2, 4, 5, 9, 10] and measurements have also been made of the first[3, 9] and second[9] overtone bands. The fundamental band of ^{15}NO has been examined with the high resolving power of a grating spectrometer.[11] Magnetic rotation spectra[13] of the 2–0 and 3–0 bands show good agreement with the absorption spectra.

The bands differ in several respects from those of simple diatomic molecules in $^1\Sigma^+$ states. The ground state of nitric oxide is a $^2\Pi$ state, which consists of two components, $^2\Pi_{3/2}$ lying about 124 cm.$^{-1}$ above $^2\Pi_{1/2}$. Only the transitions $^2\Pi_{1/2}$–$^2\Pi_{1/2}$ and $^2\Pi_{3/2}$–$^2\Pi_{3/2}$ are allowed. Each of the rotational levels of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sub-states is a close doublet (Λ-doublet). In this case, the rotational and vibrational constants for the two states are very similar, so that an infra-red band consists of the near superposition of two bands, one $^2\Pi_{1/2}$–$^2\Pi_{1/2}$, the other $^2\Pi_{3/2}$–$^2\Pi_{3/2}$. Each of these sub-bands possesses a Q-branch ($\Delta J = 0$) in addition to the P and R branches.

The infra-red spectra of samples of nitric oxide trapped at liquid helium temperatures in different matrices have been studied.[12] They indicate that nitric oxide may be trapped as monomer or as *cis*- or *trans*- dimer; the *cis* form is the more stable.

Absolute intensity measurements of the 1–0 and 2–0 bands have been made, from which the dependence of the electric moment on internuclear distance is derived.[6] Line-widths in the 1–0 band have also been measured.[7] An empirical correlation between infra-red intensities, dissociation energies and equilibrium internuclear distances has been suggested.[8]

Table IX.—Constants for the Ground State of ^{14}NO (*cm.*$^{-1}$)

	B		ΔG (0–1)
	$v=0$	$v=1$	
$^2\Pi_{3/2}$	1·7200	1·7023	1875·85
$^2\Pi_{1/2}$	1·6733	1·6561	1876·11

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RAMAN SPECTRUM

In the Raman spectrum[1–6] of gaseous nitric oxide, not only have the vibrational shift and the partly resolved rotational shifts been observed, but also the electronic shifts corresponding to the transitions[12] between the two sub-levels of the ground state, $^2\Pi_{3/2}$–$^2\Pi_{1/2}$. The degree of depolarization of the line $\Delta\nu=1876$ cm.$^{-1}$ was found[7] to be 0·31. A theoretical discussion of the intensity in such a case has been given.[8]

The Raman spectrum of liquid[9–11] and solid[11] nitric oxide is more complicated, and the liquid shows strong lines at $\Delta\nu=1861$, 262, 196 and 167 cm.$^{-1}$ and two weaker lines at $\Delta\nu=1760$ and 487 cm.$^{-1}$; strong infra-red bands lie at 1863 and 1770 cm.$^{-1}$. It is thought that these spectra arise from a dimer of nitric oxide, probably a bent ON·NO molecule.

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MICROWAVE SPECTRUM

Transitions between the components of the Λ-doubled levels of the ground state $X^2\Pi$ have been observed using the Zeemann and Stark effects in the microwave region.

Measurements of the Zeemann effect in $X^2\Pi_{1/2}$ ($J=\frac{1}{2}\rightarrow\frac{3}{2}$ and $\frac{3}{2}\rightarrow\frac{5}{2}$ for ^{14}NO[5–7, 14] and ^{15}NO[7, 14]) and in $X^2\Pi_{3/2}$ ($J=\frac{3}{2}\rightarrow\frac{5}{2}$ for ^{14}NO[1, 8, 19]) have given values for the rotational constants B and D, the Λ-type doubling constants p and q, the magnetic hyperfine structure constants, and the nuclear quadrupole moment of nitrogen. Many other theory papers have attempted to relate these constants,[2–4, 9–12, 15, 20–22] with varying degrees of success; the relation of l-uncoupling and Λ-doubling has been carefully treated.[14]

The Stark effect has been studied in $X^2\Pi_{1/2}$ ($J=\frac{1}{2}\rightarrow\frac{3}{2}$ and $\frac{3}{2}\rightarrow\frac{5}{2}$ for ^{14}NO) and the dipole moment calculated to be $0{\cdot}158\pm0{\cdot}006$ D.[16]; a theoretical paper on the Stark effect has also appeared.[17]

Another value for the dipole moment, $0{\cdot}148\pm0{\cdot}002$ D., has been derived from measurements of the non-resonant Debye-like absorption of gaseous NO at 9 and 23 kMc./sec. (0·3 and 0·8 cm.$^{-1}$) at pressures from 3 to 27 atm.[18]

The effect of structure on the magnetic properties of NO has been reviewed.[13]

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The Nitric Oxide Molecule-Ion, NO^+

One band-system of the gaseous ion NO^+, isoelectronic with N_2 and CO, has been observed. The upper state, $A^1\Pi$, is perturbed by a $^3\Sigma^-$ state, and from a study of the perturbations, some information can be obtained about the perturbing state[1–4]. The molecular constants[5] are as follow:

State	T_e	ω_e	$x_e\omega_e$	B_e	$10^2\ \alpha$	$10^6\ D$	r_e
$A^1\Pi$	73469·6	1608·9	23·3	1·587	2·4	8	$1{\cdot}192_6$
$e^3\Sigma^-$		~1150		~1·25			
$X^1\Sigma^+$	0	2377·1	16·35	2·002	2·02	6	$1{\cdot}061_9$

Two of Tanaka's Rydberg series[6] in NO appear to converge on the state $A^1\Pi$ of NO^+; two others converge on less highly excited states.

The NO^+ ion is of course well known both in the solid state and in solution. Raman shifts, $\Delta\nu \sim 2330$ cm.$^{-1}$, are observed,[7–9] close to the value $\Delta G_{1/2} = 2344{\cdot}4$ cm.$^{-1}$ for the gaseous ion. Sodium nitrite dissolved in perchloric acid solution shows a single broad maximum at 2600 A., ascribed to the charge-transfer spectrum of the NO^+ ion[10].

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Nitrogen Sesquioxide

The visible spectrum of N_2O_3 in organic solvents[3, 9, 11] is a continuum with a peak at 6250 A. and a minimum at 4500 A.; the gas is thus blue, and indeed quite a bright pure blue. In the ultra-violet the spectrum is again continuous, though diffuse bands appear between 3280 and 3840 A.[1, 2, 4] The transition giving rise to the visible absorption has been ascribed[5, 11] π–π^* character, while the near ultra-violet transition is possibly n_N–π^*. The 6250 A. peak also appears in a strong solution of HNO_2 in perchloric acid, suggesting dehydration of the acid.[8]

In the infra-red the gas,[6] solution,[12] and solid[7, 10, 13] all show bands suggesting that the stable structure is O═N—NO_2, the N–N bond being similar to that in N_2O_4, and responsible for the continuous electronic spectrum. There is evidence[10, 13] that the molecule can be trapped at low temperatures as the unstable nitrite structure O═N—O—N═O since the spectrum is like that of the unstable form of N_2O_4

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$O{=}N{-}O{-}NO_2$. The spectra of solid $^{14}N_2O_3$ and $^{15}N_2O_3$ have been investigated,[13] and all the fundamentals of the stable form assigned; it has not been proved that the molecule is planar, but most probably it is.

The Raman spectrum of a solution has been studied[14]; also Urey–Bradley potential constants have been derived.[15]

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Nitrogen Dioxide

VISIBLE AND ULTRA-VIOLET REGIONS

The absorption spectrum of nitrogen dioxide has been observed from 9000 A. down to 1080 A., but as yet no satisfactory analysis has been given of any of the bands in this region, except for various Rydberg series around 1200 A., and the parallel band at 2491 A.

The spectrum can be divided into various regions for the purposes of discussion:

(i) 9000 A.–3200 A. Bands of fantastic complexity throughout the region,[1, 9, 14] mainly red-degraded, and becoming predissociated below about 4400 A.; the strongest bands are in the blue and green. The complexity is not due to superimposed hot bands[22] (involving a vibrationally excited ground state) since, except for a shift of some 55–70 cm.$^{-1}$, there is little change in the spectrum at 1·5°K. Beyond 6200 A. a sharp decrease in intensity may indicate a second electronic transition.[22]

(ii) 2700 A.–2350 A. Red-degraded parallel bands of simpler structure,[2–4, 8, 10–13, 18] showing predissociation below 2450 A. Many inconclusive analyses of the (000 ← 000) band at 2491 A. have been made, but a recent successful partial rotational analysis,[27] using the ground state constants from microwave data, has shown that the N–O bond length increases from 1·197 A. to 1·314 A. and that the angle decreases from 134° 15′ to 121° 2′; this analysis was based on the assignment of two lines, $R(14)$ and $R(16)$ of the sub-band $K=0$, and the subsequent matching of trial and observed spectra. This transition is assigned[27] as $^1B_2 \leftarrow {}^1A_1$.

(iii) 2350 A.–2000 A. Diffuse bands[4, 12, 23] of slightly greater intensity than (ii), showing a vibrational interval,[4] presumably upper state, of 940 cm.$^{-1}$.

(iv) 2000 A.–1700 A. Continuum (with overlying weak absorption), increasing in intensity towards shorter wave-lengths.[15, 21, 23]

(v) 1700 A.–1300 A. Many bands[15, 21, 23] between 1690 A. and 1350 A. (λ_{max} 1467 A.), possibly two systems, overlying a continuum. About a hundred bands occur, which have been variously, but tentatively, assigned.

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(vi) 1300 A.–1080 A. Several strong diffuse bands,[15, 21, 23] centred around 1290 and 1150 A., and showing possible vibrational intervals of 610 and 560 cm.$^{-1}$. Two ionization potentials[23] are suggested: a first I.P. of 9·62 e.v., and a second I.P. of 11·62 e.v.

The fluorescence[5, 20] and emission[17] spectra have also been studied, as have the effect of temperature on predissociation,[7] and the effect of magnetic fields.[6] The magnetic rotation spectrum has been examined.[26]

The electronic states of the molecule have been considered,[16, 19, 24, 25] orbital energies calculated by linear combinations of atomic orbitals and molecular orbitals methods,[25] and electronic transitions assigned to the various band systems[16, 19, 23–25]; doubt still exists among various workers as to the correct assignment.[25]

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REACTIONS INVOLVING NITROGEN OXIDES

Nitric oxide reacts with atomic oxygen to give nitrogen dioxide in a process in which continuous radiation is emitted[1]:

$$NO + O \rightarrow NO_2 + h\nu$$

The maximum of intensity lies in the yellow-green region of the spectrum. The reaction provides a useful test for the presence of atomic oxygen, for example in flames.[6] This spectrum appears to be identical with that of the air afterglow.[6, 8, 11, 13, 15]

Spectra emitted in discharges through nitrogen dioxide,[2, 4] from hot nitrogen dioxide,[3] from the decomposition of ozone in presence of nitrogen,[5] from hot nitrous oxide,[7] form a high-frequency torch discharge in air[9] and from high-voltage sparks in air[10] have been examined.

Studies have also been made of the spectra of flames supported by oxides of nitrogen.[12, 14, 16]

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INFRA-RED SPECTRUM

Vibration–rotation studies[2–12] of many bands of both $^{14}NO_2$ and $^{15}NO_2$ have been made over the region 700–6000 cm.$^{-1}$, and from studies of various combination, difference[7] and fundamental[10,12] bands a complete set of vibrational constants has been given; disagreement still exists over the value of x_{22}, which can be obtained from the fundamental ν_2.[7,9–11] Force constants have also been obtained from the vibration frequencies.[10,12]

The vibrational frequencies appear to be:

	$\nu_1\ (a_1)$	$\nu_2\ (a_1)$	$\nu_3\ (b_1, \text{i.r.})$
$^{14}NO_2$	1322·5 cm.$^{-1}$	749·7 cm.$^{-1}$	1617·75 cm.$^{-1}$
$^{15}NO_2$	1312	740	1580·32

though the values of ν_1 and ν_2 differ in various papers by about 2 cm.$^{-1}$; ground state constants are given[12] as:

$^{14}NO_2$	$A = 8{\cdot}003$ cm.$^{-1}$	$B = 0{\cdot}434$	$C = 0{\cdot}412$
$^{15}NO_2$	$A = 7{\cdot}642$	$B = 0{\cdot}434$	$C = 0{\cdot}410$

while the centrifugal stretching terms for $^{14}NO_2$ are[7, 12]:

$$D_J = 0{\cdot}5 \pm 0{\cdot}1 \times 10^{-5}; \qquad D_K = 2{\cdot}9 \pm 0{\cdot}6 \times 10^{-3} \text{ cm.}^{-1}$$

The observed spectrum is consistent with a molecule of point group C_{2v}, of dimensions $r_{N-O} = 1{\cdot}197$ A.; $O\text{–}\widehat{N}\text{–}O = 134° \ 15'$ (from microwave studies). As a consequence of the zero nuclear spin of ^{16}O, half the levels are missing in $N^{16}O_2$, and an intensity alternation, predicted since levels with $K = 0$ are allowed only for even J values, has been observed.[7]

No spin-doubling[7] has been observed, though an unexplained doubling occurs in some lines of the P-branch of $2\nu_1 + \nu_2$. Various other anomalies[7] are found: at 4740 cm.$^{-1}$ where bands $3\nu_3$ and $2\nu_1 + 3\nu_2$ coincide, and at 5980 cm.$^{-1}$ where bands $\nu_1 + 3\nu_3$ and $3\nu_1 + 3\nu_2$ coincide; no explanation in terms of vibrational perturbation or Coriolis splitting is acceptable.

The bands are broader in *cyclo*hexane solution.[1] Frequencies little different from the gas-phase frequencies are observed[13] for molecules trapped in a matrix at 20°K.

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RAMAN SPECTRUM

It is practically impossible to observe the Raman spectrum of gaseous NO_2 since it absorbs light throughout the visible and ultra-violet regions; the solid is of course N_2O_4.

MICROWAVE AND FAR INFRA-RED SPECTRUM

Five microwave lines,[1–7] with magnetic hyperfine structure, have been observed, and assigned to various rotational transitions.[7] Nine more lines in the far infra-red[8] confirm the microwave rotational constants (which agree fairly well with those derived from infra-red measurements):

$$A-\tfrac{1}{2}(B+C) = 227020 \text{ mc. } (7{\cdot}573 \text{ cm.}^{-1})$$
$$\tfrac{1}{2}(B+C) = 12648{\cdot}6 \text{ mc.}$$

A large centrifugal distortion term D_K, of $-2{\cdot}24\times 10^{-3}$ cm.$^{-1}$ has been observed, and found to agree with that predicted by theory. The dimensions of the molecule, which has point group C_{2v}, are given as:

$$r_{\text{N–O}} = 1{\cdot}197 \text{ A.}; \qquad \text{angle O–N–O} = 134^\circ\, 15'$$

No electron spin fine structure has been observed.[8]

The theory of the energy levels is discussed.[9, 10]

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Dinitrogen Tetroxide

The ultra-violet spectrum[2, 3, 11, 14, 20] of dinitrogen tetroxide is continuous, and starts at 3900 A.; there is a maximum[11, 14] at 3400, a minimum[11, 14] at 3000, and a shoulder[14] at 2500 A. on the way up to a second maximum somewhere below 2000 A. The reason for the continuum is presumably the low heat of dissociation of the long weak N–N bond, which has been variously described as pure π,[16] or orthodox σ with some π character.[28] Possible electronic transitions have been worked out, and predict that the molecule could be coloured[28] (a ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition is predicted for 4500 A.), but the observed absorption coefficient is zero in the visible region.[14] Quite different absorption is found for nitrogen dioxide adsorbed on films of aromatic substances.[30]

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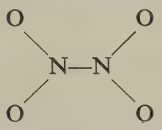
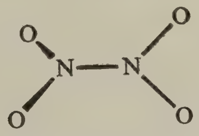
The infra-red[1, 5, 6, 8–10, 15, 18, 19, 22, 24, 26, 27] spectrum has been studied for the gas, liquid and solid, and the same bands found to appear in all three[18, 19]; eleven of the twelve fundamentals and all the combination bands observed (up to 5200 cm.$^{-1}$) have been assigned[27] from infra-red and Raman[4, 7, 12, 13, 23, 27] data for $^{14}N_2O_4$ and $^{15}N_2O_4$.[17, 26, 27] The twelfth fundamental, the inactive torsional mode, is calculated to lie at about 50 cm.$^{-1}$.[27]

The stable form of the molecule is the planar form of V_h symmetry[10, 18, 19, 27]:



rather than the non-planar form of V_d symmetry. Studies of the temperature dependence of the infra-red spectrum of the solid show that the molecule may exist in two unstable forms as well, viz., the V_d symmetry form:



and an unsymmetrical $ONONO_2$, both of which can be converted into the stable isomer by annealing.[22] This is supported by the infra-red spectrum of N_2O_4 molecules trapped in matrices at liquid helium temperatures,[24] and a table of fundamentals for these unstable isomers can be drawn up.[22, 24, 26]

The fundamental frequencies of liquid $^{14}N_2O_4$ are:

$a_g\ \nu_1$ 1379·6;	$a_u\ \nu_4$ inactive;	$b_{1g}\ \nu_5$ 1712;	$b_{1u}\ \nu_7$ 429;	$b_{2u}\ \nu_9$ 1748;	$b_{3u}\ \nu_{11}$ 1262
ν_2 808	(~50)	ν_6 482		ν_{10} 381	ν_{12} 750
ν_3 260			$b_{2g}\ \nu_8$ 622		

Urey–Bradley potential constants[25, 29] have been derived and the NO_2–N_2O_4 equilibrium has been studied spectroscopically.[21]

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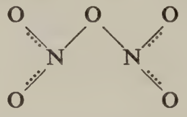
Nitrogen Pentoxide

Nitrogen pentoxide is a colourless gas, but in the ultra-violet[3,4,8] its absorption begins at about 3800 A. (where the absorption coefficient α_{10} is 0·002) and is quite strong ($\alpha_{10}=$ 0·52) at 2850 A.; no indication of a maximum before 2400A. occurs. The continuum at 3800 A. fits with:

$$N_2O_5 = N_2O_4 + O(^3P)$$

From the infra-red spectrum[1,2,11,12,13] the structure of the solid at -190°C. appears[11,12] to be $NO_2^+NO_3^-$ (as confirmed by X-ray diffraction). The active fundamentals can be assigned by comparison with nitrate salts and CO_2, while the others can be obtained from the Raman spectrum[5,6,7]: NO_2^+ 1400, 538, 2375 cm.$^{-1}$; NO_3^- 1050, 824, 1413, 722 cm.$^{-1}$ (^{14}N). The isotopic shift $^{14}N-{}^{15}N$ has been used to confirm this. At liquid helium temperature, N_2O_5 trapped in a matrix of solid CO_2 is covalent,



its spectrum showing the characteristic frequencies of the nitro group, split as a result of the in- and out-of-plane combinations of the two NO_2 groups. The frequencies are then $1752+1700$, $1316+1248$ and $737+719$, which can be compared with the spectrum of the gas,[13] where the bands characteristic of the nitro group again appear (and indicate this structure for the gas): asymmetric stretch 1720 cm.$^{-1}$, symmetric stretch 1240 cm.$^{-1}$ and O–N–O bend 730 cm.$^{-1}$.

An atmospheric band at $7{\cdot}7\mu$ is ascribed to N_2O_5.[9,10]

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Nitrogen Trioxide

The extremely intense banded absorption occurring in the region, 5000 to 7100 A., observed on evaporating N_2O_5 into ozone,[1] is ascribed on kinetic grounds[1,2] to NO_3. Under high resolution the whole system is seen to be predissociated.[3] The

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colour of the gas is a very pure bright blue, much more intense than the chalky violet-blue colour of ozone, and not unlike that of N_2O_3.

The molecule is predicted to be planar[4] in its ground state.

References

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Nitrosyl Fluoride

A vibrational analysis of eighteen bands in the near ultra-violet absorption spectrum[1, 2] gives upper state vibrational frequencies:

$$\nu_1 = 1450\ \text{cm.}^{-1}; \quad \nu_2 = 343; \quad \nu_3 = 1086$$

Infra-red studies of twelve bands[4] have given ground state vibrational frequencies:

$$\nu_1\,(\text{N–O}) = 1844{\cdot}03\ \text{cm.}^{-1}; \quad \nu_2\,(\text{bending}) = 521; \quad \nu_3\,(\text{N–F}) = 765{\cdot}85$$

An analysis of the rotational structure of the ν_1 and ν_3 bands[5, 6] gave rotational constants for the two bands, in fair agreement with the results of microwave studies[3,6] of three rotational lines.

The dipole moment is calculated from the microwave spectrum[3] to be 1·81 D. Force constants and thermodynamic properties have been calculated.[7]

$$r_{\text{N–O}} = 1{\cdot}13\ \text{A.}; \quad r_{\text{N–F}} = 1{\cdot}52\ \text{A.}; \quad \alpha = 110{\cdot}2^\circ$$

References

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Nitrosyl Chloride

Studies of the infra-red spectrum[1, 5–8, 10, 11] of the vapour of nitrosyl chloride show that the fundamental frequencies are as follow:

$$\nu_1 = 329\ \text{cm.}^{-1}; \quad \nu_2 = 593; \quad \nu_3 = 1800$$

A determination of the structure of the molecule from the incompletely-resolved infra-red bands[7] is in satisfactory agreement with the results of observations on the $J = 2 \leftarrow 1$ transition in the microwave region,[9] and the much more complete account of the microwave spectrum given by Millen and Pannell,[12] who used the isotopic species $N^{16}O^{35}Cl$, $N^{16}O^{37}Cl$ and $N^{18}O^{35}Cl$. (See also refs. 13 and 14.)

The following structure is obtained[12]:

$$r\,(\text{N–O}) = 1{\cdot}139\ \text{A.}; \quad r\,(\text{N–Cl}) = 1{\cdot}978\ \text{A.}; \quad \text{angle O–N–Cl} = 113^\circ\ 20'$$

The molecular constants have been discussed in relation to the statistical calculation[2, 8] of the gaseous equilibrium:

$$2NOCl \rightleftharpoons 2NO + Cl_2$$

Refs. p. 522

The absorption spectrum in the ultra-violet,[3, 11] and in the vacuum ultra-violet[4] region, has also been examined.

References

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Nitrosyl Bromide

A study of the infra-red spectrum[1] of the vapour of nitrosyl bromide reveals three fundamental frequencies, at 1801, 542 and 265 cm.$^{-1}$. The microwave transition $J = 2 \rightarrow 3$ has been analysed, giving rotational and quadrupole coupling constants,[2] while studies of the Stark effect in the same transition give a value 1·80 D. for the dipole moment.[3]

References

1 Burns, W. G. & Bernstein, H. J., *J. Chem. Phys.*, 1950, **18**, 1669–73 (*45*, 6057)
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Nitryl Fluoride

The infra-red spectrum of nitryl fluoride vapour and the Raman spectrum of the liquid have been investigated[2]; vibrational frequencies are given as follow:

$$\nu_1\,(a_1)\ 1312\ \text{cm.}^{-1};\quad \nu_2\,(a_1)\ 822;\quad \nu_3\,(a_1)\ 460;\quad \nu_4\,(b_1)\ 1793;$$
$$\nu_5\,(b_1)\ 570;\quad \nu_6\,(b_2)\ 742$$

assuming a Y-shaped molecule, with the fluorine atom bonded to nitrogen.[3]

Eight lines in the microwave spectrum have been identified[1] and assigned on the basis of a planar Y-shaped C_{2v} molecule; the planarity follows since the B, or anti-symmetric, rotational levels are missing. The dipole moment is calculated to be 0·47 D.

Assuming the angle O–N–O to be 125°, the dimensions[1, 2] are:

$$r\,(\text{N–O}) = 1{\cdot}23\ \text{A.};\quad r\,(\text{N–F}) = 1{\cdot}35\ \text{A.}$$

References

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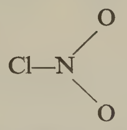
Nitryl Chloride

The six fundamental vibration frequencies[1, 2] have been observed in studies of the infra-red and Raman spectra of this molecule; these are consistent with a molecule of structure:



but do not distinguish between planar and pyramidal models.[2]

$\nu_1\,(a_1)$ 1293 cm.$^{-1}$; $\nu_2\,(a_1)$ 794; $\nu_3\,(a_1)$ 651; $\nu_4\,(b_1)$ 1685
$\nu_5\,(b_1)$ 367; $\nu_6\,(b_2)$ 411

Observations of the microwave spectrum of this molecule[3, 4] show that it is planar and Y-shaped, with r (N–Cl) = 1·83 A.; r (N–O) = 1·21 A. and angle O–N–O = 129·5°. The dipole moment, determined from the Stark effect, is 0·42 D.

References

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3 Millen, D. J. & Sinnott, K. M., *Chem. and Ind.*, 1955, 538; *J.C.S.*, 1958, 350	(*52*, 5976)
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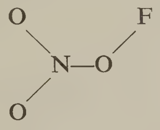
Nitroxyl Fluoride (Fluorine Nitrate)

Vibrational analysis of bands in the infra-red[1, 2] indicates a structure:



by analogy with the bands of NO_3Cl^2. The strongest bands are the NO_2 asymmetric and symmetric stretching frequencies (1776 and 1310 cm.$^{-1}$).

References

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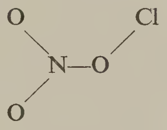
Nitroxyl Chloride

Vibrational studies in the infra-red[1] suggest that for several reasons the structure of the molecule must be regarded as the planar



rather than Cl·NO_3, the most cogent being that asymmetric top bands of all three types, *A*, *B* and *C*, are found. In the vapour the strongest bands lie at 1739, 1294 and 809 cm.$^{-1}$, and these are slightly displaced on solution in CCl_4.

Reference

1 Brändle, K., Schmeisser, M. & Lüttke, W., *Chem. Ber.*, 1960, **93**, 2300	(*55*, 1182)

Nitrogen Trifluoride

In the ultra-violet region[1] the long wave-length limit of absorption is at about 960 A., in agreement with the lowest I.P. of the molecule, 106,480 cm.$^{-1}$. The absorption coefficient decreases to zero at 1800 A., with no indication of even partly resolved electronic transitions.

The vibration–rotation spectrum in the infra-red[2–7] and Raman[7] regions has also been examined. Measurements of the absolute intensities of the fundamental bands[5] have been discussed in terms of the N–F bond moment, μ, its derivative $\delta\mu/\delta r$ and the unshared pair moment on the nitrogen atom. A potential function has also been determined.[6] The infra-red frequencies are: $\nu_1\ (a_1) = 1031$ cm.$^{-1}$; $\nu_2\ (a_1) = 642$; $\nu_3\ (e) = 907$; $\nu_4\ (e) = 497$; in the liquid the corresponding Raman shifts are ν_1 1050, ν_2 667, ν_3 905, ν_4 515 cm^{-1}.

Several investigations of the spectrum of NF_3 in the microwave region have been reported.[8–11] From observations[8] on both $^{14}NF_3$ and $^{15}NF_3$, the N–F distance is found to be 1·371 A., and the F–N–F angle 102° 9′. Measurements of the Stark effect[10, 11] lead to a value of the dipole moment of 0·234 ± 0·004 D.

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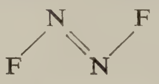
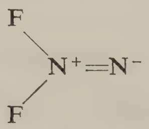
Difluorodiazine

Infra-red studies[1] of the two isomers of this substance have suggested that the lower-boiling isomer is the planar *trans*-1:2-difluorodiazine:



and that the less stable isomer is not the *cis*-form but 1:1-difluorodiazine



from the similarity of the vibration frequencies to those found in COF_2. This assignment is very much in doubt, however,[2] and the structure of the less stable higher boiling isomer must be considered as not proved until further chemical evidence is forthcoming.[3] The main point against the 1:1- structure is its lack of microwave spectrum[1, 2] (i.e., no dipole moment), which tends to rule it out unless the balancing of charges is very fortuitous.[2]

References

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Tetrafluorohydrazine

A preliminary report of the microwave spectrum of this substance has been given.[1] The observed rotational constants are consistent with a hydrazine-like model (Point Group C_2). The dipole moment is about 0·26 D.

Reference

1 Lide, D. R. & Mann, D. E., *J. Chem. Phys.*, 1959, **31**, 1129–30 (*54*, 7338)

Nitrogen Difluoride

This substance, formed by thermal dissociation of N_2F_4, has been investigated in the infra-red.[1] The band at 1074·3 cm.$^{-1}$ is ascribed to ν_1, and absorption at 930–940 cm.$^{-1}$ to ν_3; rotational analysis gives $r_{N-F} = 1{\cdot}37$ A., angle F–N–F = 104·2°.

Reference

1 Harmony, M. D., Myers, R. J., Schoen, L. J., Lide, D. R., Jr. & Mann, D. E., *J. Chem. Phys.*, 1961, **35**, 1129–30 (*56*, 5545)

Chloramine, Dichloramine and Nitrogen Trichloride

The infra-red spectra of these three compounds have only been studied once, and as they were all treated in the same paper,[1] it will be convenient to consider them together.

Chloramine, NH_2Cl, and dichloramine, $NHCl_2$, should each show six fundamentals, four of symmetry type a' and two of type a'', giving rise respectively to 'hybrid' and 'perpendicular' bands. In chloramine only ν_5, at 3380 cm.$^{-1}$, can be immediately assigned because of its pure perpendicular character, but the frequencies ν_2, ν_3 and ν_4 have also been seen, and ν_1 has been found in combination bands; ν_6 has not been observed at all. Some rotational structure has been analysed for NH_2Cl and NHDCl, and as these molecules are very nearly symmetric tops, only the broadening of three maxima shows their asymmetry. For dichloramine the position is somewhat similar: all the frequencies except ν_4 have been seen, and three overtones as well; the rotational structure shows considerable asymmetry. The resolution of the rotational fine structure was not sufficient to determine accurate constants, and tentative angles are:

NH_2Cl: angle H–N–Cl 102°; $NHCl_2$: angle Cl–N–Cl 106°

For nitrogen trichloride two fundamental bands and an overtone band have been observed but not assigned.

Reference

1 Moore, G. E. & Badger, R. M., *J.A.C.S.*, 1952, **74**, 6076–80 (*47*, 3697)

SECTION XXXV

TABLE OF NITROGEN ISOTOPES

BY C. J. L. LOCK

At present six isotopes of nitrogen are known, of which two are stable. The other four are relatively short-lived, having half-lives shorter than ten minutes. It seems unlikely that any isotopes of mass number less than twelve will be discovered. Russian workers[202, 203] have examined the stability of ^{11}N theoretically and conclude that it will be unstable to proton emission and will not have a detectable existence.

Zeldovick[204] and other workers[203, 205] consider that nitrogen isotopes in the range ^{18}N–^{21}N should be stable to neutron emission, and since β half-lives are usually $\geqslant 0{\cdot}1$ s. (^{12}N is one of the interesting exceptions to this rule) it should be possible to detect such isotopes if they are formed.

These workers consider that the limiting factor in the existence of these nuclei is their stability towards neutron emission. They argue that in a series of nuclei of constant Z, the binding energy of the $2m+2$ neutron is always greater than that of the $2m+1$ neutron because of the extra stability gained in neutron pairing. Therefore if ^{16}N, ^{18}N, and ^{20}N can exist so can ^{17}N, ^{19}N, and ^{21}N. If the series of nuclei has a closed proton shell, within any neutron shell the binding energy of each neutron added in the $2m+1$ series differs little from all the others added in that series, and similarly for the $2m+2$ series. The binding energy will drop sharply, however, on passing to the next neutron shell. Consider the filling of the $f_{7/2}$ neutron shell outside the closed shell ^{40}Ca core:

$$^{41}_{1}E = 8{\cdot}3, \quad ^{42}_{2}E = 11{\cdot}4, \quad ^{43}_{3}E = 8{\cdot}0, \quad ^{44}_{4}E = 11{\cdot}4, \quad ^{45}_{5}E = 7{\cdot}4, \quad ^{46}_{6}E = 11{\cdot}0(?),$$

$$^{47}_{7}E = 6{\cdot}8(?) \quad ^{48}_{8}E = 10{\cdot}8, \quad \text{but} \quad {}_{8}{}^{49}_{+1}E = 5{\cdot}1$$

$^{m}_{n}E$ is the binding energy of the nth neutron to be added to a neutron shell containing in all n neutrons, where the number of nucleons in the nucleus is m, and the energy is in Mev.

If the proton shell is not filled, i.e. there are excess protons, the binding energy drops sharply within the range of a given neutron shell; we may imagine that the first neutrons unite in pairs with the 'free' protons (those outside the closed shells), and later neutrons can no longer do this. As an example consider the binding energy of neutrons added to the ^{18}Ne core, a nucleus with two protons beyond a closed shell. We have:

$$^{19}_{1}E = 11{\cdot}4, \; ^{20}_{2}E = 16{\cdot}9, \; ^{21}_{3}E = 6{\cdot}8, \; ^{22}_{4}E = 10{\cdot}5, \; ^{23}_{5}E = 5{\cdot}2, \; ^{24}_{6}E = 8{\cdot}9$$

If the proton shell falls short of being closed by one or two protons, the binding energy of the neutrons is decreased as compared with the binding energy to a closed proton shell. But within the limits of a given neutron shell (on a core with holes in the proton shell) the binding energy varies very little for alternate neutrons, in contradistinction to the case in which excess protons are present. Consider the filling of the $f_{7/2}$ shell on a ^{39}K or ^{38}Ar core and compare with figures given above for ^{40}Ca.

$$^{39}\text{K} \quad ^{40}_{1}E = 7{\cdot}9, \; ^{41}_{2}E = 10{\cdot}0, \; ^{42}_{3}E = 7{\cdot}4, \; ^{43}_{4}E = 10{\cdot}8$$

$$^{38}\text{Ar} \quad ^{39}_{1}E = 6{\cdot}7, \; ^{40}_{2}E = 9{\cdot}7, \; ^{41}_{3}E = 6{\cdot}1$$

Applying these rules to the $d_{5/2}$ neutron shell on a ^{15}N core, the existence of ^{16}N $({}^{16}_{1}E=2{\cdot}50)$ and ^{17}N $({}^{17}_{2}E=5{\cdot}84)$ guarantees the possibility of filling the entire $d_{5/2}$ shell to ^{21}N.

An alternative method of deriving the probable upper limit of stability of nitrogen isotopes is based on the empirical relation $(N/A)_{\max}$ which is approximately 0·66 for light isotopes, where N is the neutron number, and A the mass number. Examples of nuclides obeying this relationship are ^{3}H, ^{9}He, ^{9}Li. It was thought that the factor was lower[204] for nuclei of larger mass, e.g. for ^{240}U, the highest reported isotope of uranium,[206] $N/A=0{\cdot}617$. However, the fact that ^{255}U $(N/A=0{\cdot}64)$ must have existed in the hydrogen bomb explosion 'Mike' suggests that this reduction may not be very great.[207] Applying the rule to nitrogen we find that ^{21}N is the isotope for which $(N/A)_{\max}=0{\cdot}66$.

While these nuclei may be sufficiently stable theoretically to have a detectable separate existence, their preparation will prove difficult, if not impossible. Because of the short half-lives of ^{16}N and ^{17}N successive (n,γ) reactions on ^{15}N are unlikely to give these species in measurable yield unless very high neutron fluxes are used, such as exist in a nuclear explosion[207] or in some of the newer neutron sources.[208] Because of the difficulties of sample collection the former is not likely to be of any serious use, and unless the capture cross-sections for ^{16}N and ^{17}N should prove to be very high, the fluxes which can be obtained with the best machines available are still not sufficient.

Other reactions which might yield the isotopes ^{18}N–^{21}N are analogous to those used for preparing other nitrogen isotopes.

(1) Spallation of higher elements initiated by protons or neutrons.
(2) Photospallation of higher elements.
(3) Nuclear reactions such as

$$^{18}\mathrm{O}(n,p)^{18}\mathrm{N}$$
$$^{10}\mathrm{Be}(^{10}\mathrm{Be},p)^{19}\mathrm{N}$$
$$^{10}\mathrm{Be}(^{10}\mathrm{Be},d)^{18}\mathrm{N}$$
$$^{21}\mathrm{Ne}(\gamma,3p)^{18}\mathrm{N}$$
$$^{22}\mathrm{Ne}(\gamma,3p)^{19}\mathrm{N}$$

As all these reactions will give rise to many other products as well, and the desired nitrogen isotopes will be of short half-life, the task of detecting the required products may well prove impossible.

The properties of the known isotopes of nitrogen are summarized in the Table. Most of the sections are self-explanatory but the following notes are added as a guide to the Table.

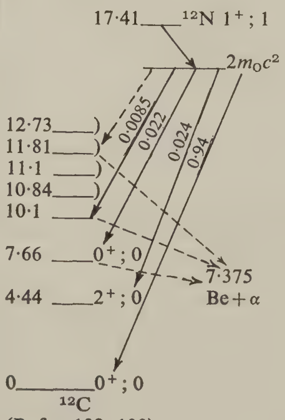
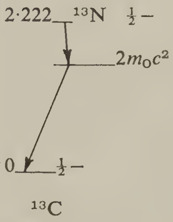
A. Section 3. All the nuclear masses quoted in the references have been converted to the new scale of nuclear masses used by the International Union of Pure and Applied Chemistry, namely $^{12}\mathrm{C}=12{\cdot}0000000$ a.m.u.

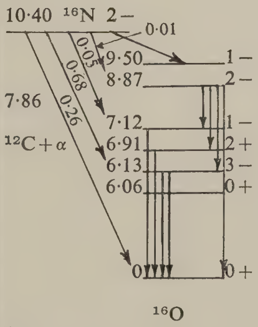
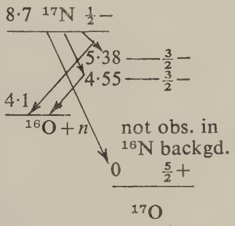
B. Section 4. Although the nuclear spin for the ground state is known with reasonable certainty for all the isotopes of nitrogen, the values are given only for those isotopes for which it has been definitely established by experiment. The units are $(h/2\pi)$. The value of the magnetic dipole moment μ is given in units of nuclear magnetons. The value is given without diamagnetic correction. The symbols R and M refer to the method of measurement, namely nuclear magnetic resonance or atomic or molecular beam spectroscopy. The nuclear quadrupole moment, q, is given in units of barns (10^{-24} cm.^{2}), and was measured by microwave absorption.

C. Section 6. The energies of particles and photons are included. The relative intensities are given in brackets after the energy of the particle or photon in one of two ways. If a % sign is given the values are absolute percentages. If the % sign is not given, the values are expressed relative to the most

Property of Isotope	^{12}N	^{13}N	^{14}N
Half-life	0·0125 s.[1,2] 0·0121 s.[3] 0·01143 s.[3,4] 0·01095 s.[5]	10·13 m.[6] 10·1 m.[7] 10·08 m.[8] 10·05 m.[9] 9·97 m.[10] 9·96 m.[11,12,13] 9·93 m.[14,15,16] 9·2 m.[17]	Stable
Type of decay or abundance	β^+; β^+, 3α[29]	β^+[30]	99·64%[31,32] 99·62%[33,34]
Mass in a.m.u. ^{12}C = 12	12·018729[38] 12·018900[39]	13·00595[40] 13·00591[41] 13·00581[42] 13·00575[42,43] 13·0057389[39]	14·00306[42] 14·00311[42] 14·003079[44] 14·003099[45] 14·003075[43] 14·00307438[39]
Nuclear spin I			1 atom. spec. microwave[52]
Magnetic moment μ			0·402 M[53] 0·40369 R[54,55] 0·40365 R[52] 0·40357 R[53]
Quadrupole moment q			+0·02[52] +0·0071[56]
Methods of preparation	$^{10}\mathrm{B}(^{3}\mathrm{He}, n)$[5,57] $^{12}\mathrm{C}(p, n)$[1,29] $^{14}\mathrm{N}(\gamma, 2n)$[2,58]	$^{9}\mathrm{Be}(^{6}\mathrm{Li}, 2n)$[3] $^{10}\mathrm{B}(\alpha, n)$[59–61] $^{12}\mathrm{C}(^{3}\mathrm{He}, d)$[62] $^{12}\mathrm{C}(d, n)$[8,30,67b,63–66] $^{12}\mathrm{C}(p, \gamma)$[67ab,68] $^{13}\mathrm{C}(^{3}\mathrm{He}, t)$[3] $^{13}\mathrm{C}(p, n)$[41,69,70] $^{14}\mathrm{N}(^{14}\mathrm{N}, ^{15}\mathrm{N})$[71] $^{14}\mathrm{N}(d, t)$[72] $^{14}\mathrm{N}(n, 2n)$[15,17,73] $^{14}\mathrm{N}(p, d)$[3] $^{14}\mathrm{N}(\gamma, n)$[7,13,17,74] $^{16}\mathrm{O}(n, p3n)$[15] $^{16}\mathrm{O}(p, \alpha)$[75] $^{16}\mathrm{O}(\gamma, p2n)$[76] $^{16}\mathrm{O}(\gamma, t)$[77,78] $\mathrm{Al}(p, \mathrm{spall})$[79–82] $\mathrm{Al}(n, \mathrm{spall})$[83]	Isotope sepn. $^{9}\mathrm{Be}(^{6}\mathrm{Li}, n)$[84] $^{9}\mathrm{Be}(^{7}\mathrm{Li}, 2n)$[84] $^{10}\mathrm{B}(^{6}\mathrm{Li}, pn)$[84] $^{10}\mathrm{B}(^{7}\mathrm{Li}, p2n)$[84] $^{11}\mathrm{B}(\alpha, n)$[85] $^{12}\mathrm{C}(^{6}\mathrm{Li}, \alpha)$[86] $^{12}\mathrm{C}(\alpha, d)$[87] $^{12}\mathrm{C}(^{3}\mathrm{He}, p)$[88,89] $^{12}\mathrm{C}(d, \gamma)$[3] $^{13}\mathrm{C}(d, n)$[90–92] $^{13}\mathrm{C}(p, \gamma)$[93–96] $^{14}\mathrm{C}(p, n)$[97] $^{14}\mathrm{C}(\beta^-)$[3] $^{15}\mathrm{N}(^{3}\mathrm{He}, \alpha)$[98] $^{15}\mathrm{N}(p, d)$[3] $^{14}\mathrm{O}(\beta^+)$[3] $^{16}\mathrm{O}(d, \alpha)$[99] $^{17}\mathrm{O}(p, \alpha)$[3]
Energy of α radiation	4, total of 3α's[29] (branch ratio $4{\cdot}4 \times 10^{-3}$)		
β^+, β^-	16·6 abs.[1] 16·37 spec.[4] 16·43 spec.[57,131] 16·384 (94%) 12·0 (2·4%) 8·7 (2·2%) 7·3 (0·85%) Others spec.[132] 16·43 (95%) 12·0 (2·4%) 8·8 (0·3%) '10·1' Others spec.[133]	1·28 spec.[40] 1·25 spec.[134] 1·24 spec.[135] 1·22 spec.[136] 1·20 spec.[137,138] 1·19 spec.[11] Others[139,140,141]	

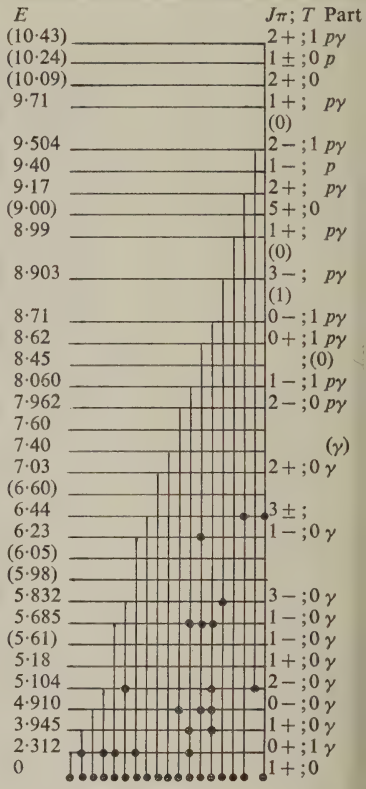
^{15}N	^{16}N	^{17}N	Property of Isotope
Stable	7·38 s.[18] 7·37 s.[3] 7·352 s.[19] 7·35 s.[20] 7·31 s.[21]	4·6 s.[22] 4·15 s.[23,24] 4·14 s.[25,26] 4·13 s.[27,28]	Half-life
0·36%[31,32] 0·38%[33,34]	β^- [35,36] β^-, α[37]	β^-, n[27]	Type of decay or abundance
15·000165[46] 15·000135[45] 15·000114[43] 15·000118[44] 15·0001081[39]	16·00612[47] 16·00607[48] 16·00601[49] 16·006089[39]	17·00844[49] 17·00847[50] 17·008449[51] 17·008580[39]	Mass in a.m.u. ^{12}C = 12
½ atom. spec.[52] −0·280 *M*[53] −0·28312 *R*[54,55] −0·28299 *R*[52] −0·28295 *R*[53] −0·28305 *R*[54]			Nuclear spin *I* Magnetic moment μ Quadrupole moment q
Isotope sepn. ^{10}B(^{6}Li, p)[84] ^{10}B(^{7}Li, pn)[84] ^{9}Be(^{7}Li, n)[84] ^{11}B(α, n)[3] ^{12}C(^{7}Li, α)[86] ^{12}C(α, p)[100,101] ^{13}C(^{3}He, p)[102] ^{13}C(t, n)[103] ^{14}C(d, n)[104] ^{14}C(p, γ)[105] ^{15}C(β^-)[106] ^{14}N(t, np)[107] ^{14}N(d, p)[84,108–110] ^{14}N(n, γ)[111] ^{15}O(β^+)[85] ^{16}O(t, α)[3] ^{16}O(p, $2p$)[3] ^{16}O(n, d)[3] ^{16}O(γ, p)[112] ^{17}O(d, α)[113] ^{18}O(p, α)[114]	^{14}C(d, γ)[3] ^{14}N(t, p)[115] ^{15}N(n, γ)[47,116,117] ^{15}N(d, p)[64,68,118–121] ^{16}O(n, p)[18,122] ^{18}O(d, α)[48,119] ^{19}F(n, α)[35,36,123–126] LiF(^{14}N, spall)[127] Cu(^{14}N, spall)[127] Al(^{14}N, spall)[127]	^{11}B(Li^7, p)[50] ^{14}C(α, p)[22,25,49] ^{17}O(n, p)[49] ^{18}O(γ, p)[23,128] ^{18}O(t, α)[51,129] ^{19}F(γ, $2p$)[3] spall. Al with ^{14}N, ^{15}N, ^{16}O, ^{16}N, ^{20}Ne[130], ^{16}O[24], γ[121] spall. Ta with ^{14}N, ^{15}N, ^{16}O, ^{16}N, ^{20}Ne[130] photonuclear decomp. of H_2O, O, LiF, Ne, Mg, Al, Cu[128] Li_2CO_3 bombard. with ^{15}N, ^{16}O[24]	Methods of preparation
		1·72 from 9·58 Mev state of ^{16}O[37]	Energy of α radiation
	10·40(28%) 4·39 (54%) 3·32 (19%) spec.[120] 10·3 (18%) 4·27 (55%) 3·28 (21%) spec.[142] ~10·3 (~20%) ~4·3 (~40%) ~3·8 (~40%) cl. ch.[20] 10·40 (28%) also 4·39[143] 10·4 (26%) 4·3 (68%) 3·3 (4·9%) 1·5 (1·1%) pair coinc. spec.[144] Others[37,145–149]	3·7 recoil, coinc. abs.[150] 4·2, 3·3 spec.[151]	β^+, β^-

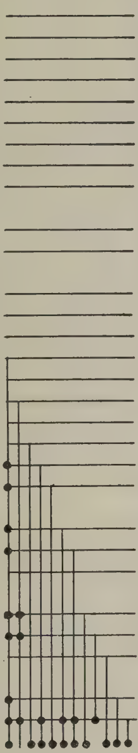
Property of Isotope	^{12}N	^{13}N	^{14}N
n			
γ		No $\gamma > 0{\cdot}135$, $< 0{\cdot}70$[141, 152, 153] $0{\cdot}280\gamma$, $\gamma/\beta^+ = 0{\cdot}20$[137] 0·515 annihil. rad. but no $0{\cdot}280\gamma$[6]	2·313 level ^{14}N, $t_{\frac{1}{2}} = 2 \times 10^{-13}$s. Doppl broadening[154] $7{\cdot}3 \times 10^{-14}$s.[155]
Disintegration energy and scheme	$Q_{\mathrm{ec}} = 17{\cdot}7$[162] $Q_{\mathrm{ec}} = 17{\cdot}6$[1, 163] $Q_{\mathrm{ec}} = 17{\cdot}45$[57, 131, 133] $Q_{\mathrm{ec}} = 17{\cdot}40$[132] $Q_{\mathrm{ec}} = 17{\cdot}39$[4]	$Q_{\mathrm{ec}} = 2{\cdot}27$[134] $Q_{\mathrm{ec}} = 2{\cdot}26$[6, 135] $Q_{\mathrm{ec}} = 2{\cdot}24$[136] $Q_{\mathrm{ec}} = 2{\cdot}222$[3, 138, 162, 164] $Q_{\mathrm{ec}} = 2{\cdot}22$[137] $Q_{\mathrm{ec}} = 2{\cdot}21$[11]	
	 17·41 ¹²N 1⁺; 1 2m₀c² 0·0085 0·022 0·024 0·94 12·73 11·81 11·1 10·84 10·1 7·66 0⁺; 0 4·44 2⁺; 0 7·375 Be + α 0 0⁺; 0 ¹²C (Refs.: 132, 133)	 (Ref.: 3)	

^{15}N	^{16}N	^{17}N	Property of Isotope
		0·9 (^{16}O recoil cl. ch.)^{150}. 1·0 broad (p recoil cl. ch.)^{26} 1·22, 0·426 ratio $n_1/n_2=1{\cdot}6$ spec.^{151}	n
	γ_1 61·3(100) γ_2 7·10(8) pair spec.^{156} scint. spec.^{157} γ_1(100) γ_2 7·12 (7)scint. spec.^{122} γ_1(100) γ_3 1·72 (0·15) γ_4 1·90 (0·05) γ_5 2·75 (1·3) γ_2 coinc. with γ_3, γ_4 γ_1 coinc. γ_5 scint. spec.^{158} γ_5 (1·3) 8·88 (0·11) ^{19}F $(p, \alpha)^{159}$ γ_5 (1·3) 8·87 (0·09) ^{19}F $(p, \alpha)^{160}$ Others$^{144-146, 161, 162}$		γ
	$Q_\beta=10{\cdot}402^{3}$ $Q_\beta=10{\cdot}40^{120, 143, 144, 149, 158, 162}$ $Q_\beta=10{\cdot}33^{142}$ $Q_\beta=10{\cdot}3^{146}$	$Q_\beta=8{\cdot}8^{162, 163}$ $Q_\beta=8{\cdot}71^{151}$ $Q_\beta=8{\cdot}7^{150}$	Disintegration energy and scheme
	 10·40 ¹⁶N 2− 0·01 0·05 0·68 0·26 9·50 1− 8·87 2− 7·86 ¹²C+α 7·12 1− 6·91 2+ 6·13 3− 6·06 0+ 0 0+ ¹⁶O (Refs.: 3, 20, 37, 120, 122, 142–146, 148, 149, 156–158, 161, 162, 165, 166)	 8·7 ¹⁷N ½− 5·38 3/2− 4·55 3/2− 4·1 ¹⁶O+n not obs. in ¹⁶N backgd. 0 5/2+ ¹⁷O (Refs.: 3, 150, 151)	

Property of Isotope	^{12}N		^{13}N			^{14}N		
	E	$J\pi$; *T*	*E*	$J\pi$; *T*	Part.	*E*	$J\pi$; *T*	Part
Nuclear levels of isotopes including energy, quant. nos. *J*, π, *T* where known, observed transitions and particles emitted from each level	3·46		25·2		*p*, ^{3}He	18·1		
	3·18		24·8		*p*, ^{3}He	17·0		
			24·5		*p*, ^{3}He	16·1		
	2·35		23·2		*p*, ^{3}He	15·6		
	(1·97)		22·8		*p*	15·44		*npαd*
	1·56					15·14		*npαd*
	1·06		19·5			14·84		*npαd*
						14·43		*pαd*
	0	1^+;	16·6		*p*	14·3		
						14·22		*pαd*
	(Refs.: 3, 38, 167)		15·2			14·18		
						14·10		
			13·2			14·03		
			12·1		*p*	(13·93)		
			11·6		*p*	13·82		
			10·38	$\frac{7}{2}-$;		13·71	3;	*npαd*
			9·48	$\frac{7}{2}-$;		13·66		
			8·89	$\frac{1}{2}-$;		13·61		
			8·10	$\frac{3}{2}+$;	*p*	13·58		
			7·415	$\frac{5}{2}+$;	*p*	13·55		
			7·19	$\frac{1}{2}+$;	*p*	13·43		
			6·908	$\frac{3}{2}-$;	*p*	13·28		
			6·60	$\frac{1}{2}+$;	*p*	13·22		*npα*
			6·379	$\frac{5}{2}+$;	*p*	13·19		
						13·16	0 −;	*npαd*
							1 −;	
						12·92	4 +;	*pαd*
			3·555	$\frac{5}{2}+$;	*γ*	12·86		
			3·507	$\frac{3}{2}-$;	*pγ*	12·82	4 −;	*pαdn*
						12·80	4 +;	*npαd*
			2·365	$\frac{1}{2}+$;	*pnγ*	12·73		
						12·67	3 −;	*npαd*
						12·61	3 +;	*pαd*
						12·56		
			0	$\frac{1}{2}-$;	β^+	12·51		*pαd*
			(Refs.: 3, 16, 65, 85, 160, 168–173)			12·48		
						12·44	4 −;	*pαd*
						12·41		
						12·39		
						12·29		*pα*
						12·19		*pn*
						(12·08)		*pn*
						(12·04)		
						11·95		*pn*
						11·84		
						11·83		
						11·80		
						11·76	1 +;	*pn*
						11·67		*dp*
						11·50	3 +;	*dp*
						11·48		
						11·38	1 +;0	*dpn*
						11·30		
						11·26	2 −;0	*dpn*
						11·24	3 −;1	*dpn*
						11·07	1 +;0	*dpn*
						10·83	1 −;	
						(10·57)	1 +;	*dp*

^{15}N			^{16}N			^{17}N			Property of Isotope
E	$J\pi; T$	Part.	E	$J\pi; T$	Part.	E	$J\pi; T$	Part.	
19·16		nd	12·99	2 − ;		4·18			Nuclear levels of isotopes including energy, quant. nos. J, π, T where known, observed transitions and particles emitted from each level
18·28		npαd	12·8		dp	4·01			
18·09		pdt	12·62		dp	(3·86)			
17·72		pαdt	12·51	2 − ;		3·65			
17·70		dnα	11·45	(3 − ; 1)		3·57			
17·58		td	11·2	2;	dp	3·27			
17·37		pαtdn	10·77	(3 − ; 1)		3·212			
17·24		td	10·5			3·132			
17·11		dα	(9·8)			2·82			
16·90		nd	9·532	3 − ; 1		2·536			
16·77			9·42	(3 − ; 0)		1·906			
16·72		npd	9·36	(3 − ; 0)		1·89	$\frac{3}{2}$;		
16·67			8·86	(2 − ; 1)		1·851			
16·58			8·68	(3 − ; 1)					
16·47		p				1·324			
16·43			7·1	1 − ;					
16·38									
16·33			6·13	3 − ;		0	$\frac{1}{2}$ − ; $\frac{3}{2}$	β^-	
16·24			6·03	(3 − ; 0)					
16·21			5·526	1;		(Refs.: 3, 50, 51, 151)			
16·05		nα	5·32	(2 +, 3 +);					
15·99		nα	5·24	(2 −, 3 ±);					
15·96			5·141	(3, 4, 5, −);					
15·93		nα	5·059	(1, 2, −);					
15·92		nα	(5·01)						
15·89			4·98	2 − ;					
15·61		nα	4·88	(1 −);					
15·37		nα	4·78	(1 +, 2 −, 3 −);					
15·29		nα	4·40	1 − ;					
15·08		nα	4·32	(1 +);					
15·01		nα	3·98	(1 +, 2 +);					
14·90		nα	3·51						
14·82			3·40						
14·7			3·34						
14·63		nα							
14·51			(1·71)						
14·49			(1·29)						
14·4									
(14·33)			0·392	1 − ;					
14·25			0·295	3 − ;					
14·17		nα	0·120	0 − ;					
14·11		nα	0	2 − ; 1					
14·07		nα							
14·03			(Refs. 3, 115, 117, 119, 121, 194–201)						
13·89									
13·85		nα							
13·71		nα							
13·66									
13·61	($\frac{5}{2}$ −); $\frac{3}{2}$	nα							
13·58									
13·52									
13·42	$\frac{5}{2}$ + ; ($\frac{3}{2}$)	pα							
13·39									
13·36	$\frac{3}{2}$ − ;	nα							
13·18		npα							
13·14		npα							

Property of Isotope	^{12}N	^{13}N	^{14}N
			 E Jπ; T Part (10·43) 2+;1 pγ (10·24) 1±;0 p (10·09) 2+;0 9·71 1+; pγ (0) 9·504 2−;1 pγ 9·40 1−; p 9·17 2+; pγ (9·00) 5+;0 8·99 1+; pγ (0) 8·903 3−; pγ (1) 8·71 0−;1 pγ 8·62 0+;1 pγ 8·45 ;(0) 8·060 1−;1 pγ 7·962 2−;0 pγ 7·60 7·40 (γ) 7·03 2+;0 γ (6·60) 6·44 3±; 6·23 1−;0 γ (6·05) (5·98) 5·832 3−;0 γ 5·685 1−;0 γ (5·61) 1−;0 γ 5·18 1+;0 γ 5·104 2−;0 γ 4·910 0−;0 γ 3·945 1+;0 γ 2·312 0+;1 γ 0 1+;0 (Refs.: 3, 70, 84, 85, 87–99, 174–185)



^{15}N			^{16}N			^{17}N			Property of Isotope
E	*Jπ*; *T*	Part.	*E*	*Jπ*; *T*	Part.	*E*	*Jπ*; *T*	Part.	
12·93	$\frac{7}{2}-$;	*nα*							
12·91	$\frac{3}{2}-$;	*npα*							
12·50	$\frac{5}{2}+$;	*npα*							
12·33	$\frac{5}{2}+$;	*npα*							
12·15	$\frac{3}{2}+$;	*npα*							
12·10	$\frac{5}{2}-$;	*npα*							
11·97	$\frac{1}{2}-$;	*npα*							
11·95	$>\frac{1}{2}$;	*nα*							
11·88	$\frac{3}{2}, \frac{5}{2}, -$;	*npα*							
11·77	$\frac{3}{2}+$;	*np*							
11·61	$(\frac{1}{2}+)$; $\frac{3}{2}$	*npα*							
11·43	$\frac{1}{2}+$;	*γnp*							
11·29	$\frac{1}{2}-$;	*γnpα*							
11·24	$>\frac{1}{2}-$;	*n*							
10·82	$\frac{3}{2}-$;	*γ*							
10·71	$\frac{3}{2}\pm$;	*γ*							
10·55		*γ*							
10·07	$\leqslant\frac{5}{2}-$;	*γ*							
9·834		(*γ*)							
9·165		*γ*							
9·062	$\frac{1}{2}, \frac{3}{2}, +$;	*γ*							
8·575	$\frac{3}{2}+$;	*γ*							
8·316	$\frac{1}{2}+$;	*γ*							
7·57	$\frac{5}{2}, \frac{7}{2}, +$;	(*γ*)							
7·310	$\frac{3}{2}+$;	*γ*							
7·165	$(\frac{7}{2}+)$;	*γ*							
6·33	$\frac{3}{2}, \frac{5}{2}, -$;	*γ*							
5·305	$\frac{1}{2}+$;	*γ*							
5·283	$\frac{5}{2}+$;	*γ*							
0	$\frac{1}{2}-$;								
(Refs.: 3, 71, 84, 100–102, 105, 109, 111, 112, 160, 162, 186–193)									

abundant particle or photon which is given the value 100. The energies are all expressed in Mev. β-Particle energies correspond to the upper limits of the spectra.

Experimental methods for the measurement of the properties of particles are described as follows:

abs	absorption
spec	magnetic spectrometer
scint spec	measurement of pulses with scintillating crystal or solution
cl ch	cloud chamber, with magnetic field for β-particles
coinc abs coinc spec	beta- and gamma- coincidence counters with absorbers or spectrometers.

D. Section 7. The disintegration energy, or Q value, of a nuclear reaction is defined as the mass difference, expressed in Mev., between the initial and final states under consideration. For radioactive decay processes, Q is equal to the sum of the particle kinetic energy, nuclear recoil energy, and the energies of any gamma transitions necessary to de-excite the final nucleus to its ground state. In β^+ decay the Q value is given as Q_{ec}, to avoid ambiguity associated with the addition of $2m_0c^2$ to the positron energy. Energy-level diagrams have been drawn; these are not necessarily complete representations of the data, but include only those features which seem reasonably well established. Heights of various energy levels above ground state are indicated at the beginning of the level line and the quantum numbers J, π and T, where known, are placed after the level line.

E. Section 8. Listed in this section are the reported nuclear states of the isotope under consideration. No attempt has been made to list the manner by which they were measured but these can be found by referring to the attached references. Listed for each level are the energy (before the level line), and the quantum numbers J, π, and T, where known (after the level line). Also listed are the particles which have been observed to have been emitted from each state. Any values in brackets indicate that the values are doubtful or are calculations only. Experimentally observed gamma transitions are shown on the diagrams. All the gamma transitions from any single state are shown on one line, the dots on the line indicating states to which decay occurs.

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SECTION XXXVI

THE RADIATION CHEMISTRY OF NITROGEN AND ITS COMPOUNDS

BY G. R. A. JOHNSON

The processes by which ionizing radiation is absorbed by matter are discussed in detail elsewhere.[1, 2] They mainly involve interaction with the electrons of the molecules concerned, leading to electronic excitation and ionization and hence to chemical effects.[3] The field of investigation concerned with these effects, radiation chemistry, is a wide one and is commonly divided into branches according to the physical state of the substance which is irradiated. This division is convenient since the relative importance of the different processes which can follow the primary excitation and ionization events, and also the experimental techniques which may be used, are largely determined by the physical state of the system.[3]

The yields in radiation chemistry are customarily reported as the number of molecules produced or destroyed when 100 ev. of radiation are absorbed. This is written $G(\mathrm{X})$ or $G(-\mathrm{X})$, where X is the substance produced or destroyed.

ELECTRON IMPACT AND GAS-PHASE STUDIES

The primary electronic excitation and ionization following absorption of ionizing radiation by a gas can result in several possible events which include: (*a*) reaction of the ions or excited species with normal gas molecules, (*b*) dissociation of the primary ions or excited molecules, (*c*) reaction of the fragments of dissociation with normal gas molecules, and (*d*) neutralization of the primary and fragment ions, which may lead to dissociation and the production of active entities. For detailed discussion of these processes the reader is referred to other texts.[3–5]

The nature of the primary species produced by irradiation of a particular gas is rarely known with any certainty. Electron impact studies give useful information about the possible ionic species formed. However, caution must be exercised in making use of such information to interpret radiolytic processes. Radiolysis is usually carried out at pressures in the region of one atmosphere and, under such conditions, bimolecular reactions between ions and molecules may occur which are not necessarily apparent at the lower pressures used for electron impact studies. Thus, for ion-molecule reactions which have been studied[6] the reaction rates are such that, when the gas pressure is in the region of one atmosphere, these reactions will be favoured compared with ion-neutralization or dissociation of the excited ion.[7, 8] Photochemical and spectroscopic data are often helpful as an indication of the possible processes involving electronic excitation. It must be taken into consideration, however, that the transitions induced by ionizing radiation are not invariably identical with optically allowed transitions.[3]

There is no generally accepted method of dosimetry for gas-phase investigations and often it is difficult to assess the accuracy of dose-measurements in reported work. These facts should be borne in mind in comparing the values of radiation yields obtained in different investigations; the dose values given in the following sections are those of the investigators concerned, the units being converted, if necessary, to electron volts (1 rad $= 100$ ergs g.$^{-1} = 6{\cdot}24 \times 10^{13}$ ev. g.$^{-1}$). Often, particularly in earlier work, radiation yields are reported as ion-pair yields, $M/N =$ number of molecules changed per ion pair formed. Where possible, these have been converted to G-values ($G = 100\ M/WN$, where W is the energy in electron-volts required to give one ion pair).

(a) Nitrogen

ELECTRON IMPACT STUDIES

Electron impact studies show the first ionization potential of nitrogen to be close to 15·6 ev. and higher ionization potentials are found in the regions 16·6–16·9 ev., 18·76–18·84 ev., and at 23·53 ev.[9] These results are in agreement with known spectroscopic values, corresponding to the four known low-lying states for N_2^+: $X^2\Sigma_g^+$, $A\,^2\Pi_u$, $B\,^2\Sigma_u^+$ and $C\,^2\Sigma^+$.

The first appearance potential of N^+ is close to 24·3 ± 0·2 ev. and it has been shown that the dissociation products are formed without excess kinetic energy.[10] There is some uncertainty whether the N atoms formed at this appearance potential are in the ^4S state or the ^2D state. Electron impact results suggest strongly that the former of these possibilities is correct.[11] However, Lindholm, in studies of the ionization of nitrogen on bombardment with various atomic ions of known kinetic energy, obtained results leading to the opposite conclusion.[12] The problem has been discussed by Field and Franklin.[9]

The ions N_3^+ and N_4^+ have been found in mass spectrometric investigations using high source pressures.[13–15] In the most detailed investigation[15] the appearance potentials were found to be 15·8 ± 0·3 ev. for N_4^+ and 22·1 ± 0·5 ev. for N_3^+. The dependence of the number of N_3^+ and N_4^+ ions on the source pressure was consistent with their formation by a secondary process. It was concluded that the N_4^+ ion is probably formed in the process $N_2^+ + N_2 \rightarrow N_4^{+*}$ (vibrationally excited). Since the appearance potential of the N_3^+ ion is appreciably above that of N_2^+ and below that of N^+, it was suggested that the N_3^+ species is formed by the reaction $N_2^+ + N_2 \rightarrow N_3^+ + N$, where N_2^+ is an excited ion (possibly in the state $B\,^2\Sigma_u^+$).[13]

The doubly charged ions N_2^{++} and N^{++} have first appearance potentials of 40·3 ± 1 ev. and 44·14 ev. respectively.[9]

RADIATION-INDUCED OXIDATION OF NITROGEN

The oxidation of nitrogen, which occurs when mixtures of oxygen and nitrogen are irradiated, was first observed many years ago[16] and was the subject of several early investigations.[17, 18, 19] The process has assumed practical importance because the products from irradiated air are corrosive to metals and this factor has an influence on reactor design and operation. Also the possibility of producing nitric acid commercially by means of the radiation-induced oxidation of nitrogen has been considered.[20, 21]

Investigations in recent years have shown that the radiation-induced oxidation of nitrogen is a complicated process and is still by no means well understood. Only some features of the results obtained will be described here.

Using electrons of known energies to irradiate nitrogen–oxygen mixtures, Pshezetsky and Dmitriev[22] found that formation of nitrogen oxides occurs at a minimum electron energy of about 16 ev., corresponding to the appearance of N_2^+, and that an increase in the rate of reaction occurs at about 24 ev., presumably owing to N^+ and N formation. The results show that N_2^+ and excited N_2^{+*} species apparently play a more important rôle in the oxidation than the N^+ species. From experiments of this type it is concluded that ionization and dissociation of the oxygen are not important in the initiation of the reaction. However, initiation by excited oxygen ions, which would be formed at electron energies above 16 ev., does not appear to be ruled out by such experiments.

A study of the effect of added inert gases, helium, neon and argon, on the formation of nitrogen oxides from air shows that the energy absorbed by the rare gas is effective in initiating the oxidation.[23] The yield per unit dose absorbed by the total gas mixture is smaller in the presence of a rare gas than in a pure nitrogen–oxygen mixture. The effect with added rare gases is in the order He < Ne < Ar. Investigations of the effect of gas composition, gas pressure and temperature on the formation of nitrogen oxides have also been made by Russian workers.[24–26]

Harteck and Dondes[27–29] have made an extensive study of the products from irradiated nitrogen–oxygen mixtures. In most of this work use was made of the very high radiation-doses obtained with recoil fission fragments and the reaction products were measured only after high conversions, no attempt being made to study the initial stages of the reaction. For example, nitrogen–oxygen mixtures, at pressures of 2–13 atm., were irradiated until the rate of decomposition of the reaction products was equal to the rate of their formation.[29] It was found that irradiation of air with a dose-rate of $1{\cdot}9 \times 10^{19}$ ev. $g.^{-1}$ $min.^{-1}$ for a few months leads to the total consumption of the oxygen and, at 85°C., the final composition of the gas is 62·5% N_2, 20·3% NO_2 and 5·7% N_2O. A mixture of $N_2/O_2 = 2/1$ gave 46·5% N_2, 31·5% NO_2 and 5·5% N_2O and a mixture of $N_2/O_2 = 1/1$ gave 25% N_2, 6·4% O_2, 43·7% NO_2 and 0·48% N_2O under the same conditions. It was suggested[29] that the results obtained can be explained by the (overall) initiating processes: $N_2 \rightsquigarrow 2N$ and $O_2 \rightsquigarrow 2O$ (where $\rightsquigarrow$ signifies the process occurring as a result of radiation absorption) followed by free-radical reactions, including the following:

$$N + O_2 \rightarrow NO + O$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$N + NO_2 \rightarrow 2NO$$
$$N + NO_2 \rightarrow N_2O + O$$
$$N + NO_2 \rightarrow N_2 + 2O$$
$$NO + N \rightarrow N_2 + O$$
$$N_2O \rightsquigarrow NO + N$$
$$N_2O \rightsquigarrow N_2 + O$$

It was found to be unnecessary to include ionic species in the reaction scheme for nitrogen oxidation except insofar as they give free-radicals on neutralization. This conclusion receives some support from the work of Varney[30] who showed that nitrogen, activated in a discharge, reacts with oxygen to form nitrogen oxides, even when all ionic species are removed by an applied potential. However, the finding that the oxidation can occur by a free-radical mechanism does not necessarily exclude a simultaneous ionic process and the marked effect of trace amounts of nitrogen and nitrogen oxides on the formation of oxygen atoms from oxygen in a discharge has been tentatively attributed to ionic reactions.[31] The complete elucidation of the complex situation existing after irradiation to high conversions would seem to be out of the question at present and any mechanism based on the evidence so far obtained must be regarded as tentative.

Studies of the effects of small amounts of water vapour in the radiolytic oxidation of nitrogen have also revealed features which cannot be satisfactorily explained at present.[32, 33] The initial products from moist air (~1% water vapour), irradiated with 1·0 Mev. electrons are nitric acid ($G(HNO_3) = 2{\cdot}9$) and nitrous oxide.[33] Nitric acid formation occurs only if water vapour is present. After complete consumption of the water initially present, the nitric acid formed is destroyed and nitrogen dioxide is produced ($G(NO_2) = 5{\cdot}4$). The ozone, which is formed as an initial product, disappears just before the destruction of the nitric acid begins. Nitrogen dioxide inhibits the formation of nitric acid, nitrogen dioxide and ozone. The products are markedly dependent on the amount of oxygen in the irradiated mixture; maximum values of $G(NO_2)$, $G(HNO_3)$, $G(N_2O)$ and $G(-HNO_3)$ are found with about 15% of oxygen present and no oxidation takes place in the absence of oxygen. Clearly small amounts of water vapour can markedly affect the course of the radiation-induced oxidation of nitrogen, presumably by interaction with a primary species produced from oxygen or nitrogen.

Reactions of nitrogen induced by photo-dissociation and photo-ionization are important processes in the chemistry of the upper atmosphere and have been discussed by Massey and Potter.[34]

RADIATION-INDUCED REDUCTION OF NITROGEN

Several early workers showed that ammonia is produced by the α-particle radiolysis of mixtures of nitrogen and hydrogen.[35–37] In general, it was agreed that the yield from a stoicheiometric mixture ($3H_2:1N_2$) corresponds to $G(NH_3)$ between 0·6 and 0·9, but attempts to measure the equilibrium concentration of ammonia (i.e., the concentration at which the net rate of ammonia formation becomes zero owing to the radiation-induced back reaction of the ammonia decomposing into its constituents) gave different results in different laboratories, values between 4·7 and 13·5 mole % being reported[35–37]; in more recent work, where mixed fast neutron and gamma radiation was used, a value as high as 60·5 mole % was obtained.[38]

The most detailed investigation of the ammonia-formation reaction is that carried out by Cheek and Linnenborn.[39] The yields of ammonia from nitrogen–hydrogen mixtures irradiated with ^{60}Co γ-rays were measured. The conversions used were such that there was no appreciable back reaction of the ammonia and, therefore, the yield is directly proportional to the total radiation dose. For partial pressures of nitrogen and hydrogen of 34 and 14·6 atm. respectively and dose-rates from 0·78 to $1{\cdot}28 \times 10^{16}$ ev. ml.$^{-1}$ min.$^{-1}$, the initial $G(NH_3) = 0{\cdot}98$. For a given pressure of hydrogen, the rate of ammonia production (i.e., the yield per unit of irradiation time) is directly proportional to the pressure of nitrogen. For a given pressure of nitrogen, the rate is independent of the pressure of hydrogen as long as the latter is greater than a certain minimum value (corresponding to about 40% of the nitrogen pressure). From this, it is concluded that the active species responsible for ammonia formation is produced from the nitrogen and that the radiation energy primarily absorbed by the hydrogen plays no part in ammonia production. Using the results at varying partial pressures to calculate the yield from a stoicheiometric mixture gave $G(NH_3) = 0{\cdot}7$, in good agreement with the earlier values.[35, 36] Traces of oxygen in the irradiated mixture inhibit the formation of ammonia. Radiolysis of a mixture of nitrogen (34 atm.) and hydrogen (14·6 atm.), containing different amounts of rare gases, shows that some of the radiation energy primarily absorbed by the rare gas is transferred to the nitrogen and contributes to the ammonia yield. This contribution is greatest with krypton and xenon and somewhat less with argon and helium. It appears that the effect, at least in the cases of krypton and xenon where the ionization potentials are below that of nitrogen, must be attributable to excitation energy transfer from the absorbing rare gas to the nitrogen rather than charge transfer. The transfer process possibly involves a reaction similar to the dissociation of nitrogen by excited krypton atoms.[40]

Cheek and Linnenborn concluded that the radiation-induced formation of ammonia is due to reactions of excited nitrogen and nitrogen atoms, which are produced directly or by neutralization of primary ions. It has also been shown that uncharged species produced from nitrogen by means of an electric discharge can react with hydrogen to give ammonia.[30]

(b) Nitric Oxide

ELECTRON IMPACT STUDIES

The ionization potential for the formation of NO^+ obtained by electron impact is $9{\cdot}25 \pm 0{\cdot}02$ ev.,[41, 42] which is in good agreement with that found by photo-ionization.[43] The dissociative ionization of nitric oxide occurs by a number of processes which have been studied in detail[10, 44, 45, 42]; they may be summarized as follow[42]:

Process	*Appearance Potential*
$NO+e \rightarrow N^+(^3P)+O^-(^2P)+e$	19·55 ± 0·04
$NO+e \rightarrow N^+(^3P)+O(^3P)+2e$	21·11 ± 0·04
$NO+e \rightarrow N^+(^1D)+O(^3P)+2e$ or $\rightarrow N^+(^3P)+O(^1D)+2e$	23·03 ± 0·04
$NO+e \rightarrow O^+(^4S_0)+N(^4S_0)+2e$	20·11 ± 0·03
$NO+e \rightarrow O^-(^2P)+N(^4S)$	7·18 ± 0·06
$NO+e \rightarrow O^-(^2P)+N^+(^3P)+e$	19·5 ± 0·2

The appearance potentials of these processes are consistent with a value of 6·5 ev. for the dissociation energy of nitric oxide. With the exception of O^- ions formed by electron capture, it was not necessary to postulate that any of the ions are formed with excess kinetic energy.

NO^- is formed by electron capture in the mass spectrometer.[46] The ratio of the intensities NO^-/O^- is 3/10,000 for 25 ev. electrons and 10^{-6} mm. pressure of nitric oxide. The ratio NO^-/O^- depends on the pressure of nitric oxide since the intensity of O^- is proportional to the pressure, whilst that of NO^- is approximately proportional to the square of the pressure.

RADIATION-INDUCED DECOMPOSITION

The decomposition of nitric oxide induced by α-radiation was found by Mund and Gillerot[47] to give nitrogen and oxygen, with $G(N_2)=2{\cdot}3$. Secondary reactions lead to nitrogen dioxide and N_2O_3.

More recently some aspects of the decomposition by ^{235}U fission-fragment radiation have been studied by Harteck and Dondes.[48] Irradiation of nitric oxide at 500 mm. (70°C.) leads to decomposition with $G(-NO)=13{\cdot}8 \pm 1{\cdot}4$, $11{\cdot}4 \pm 1{\cdot}15$, $9{\cdot}5 \pm 1{\cdot}0$ for doses up to 6×10^{18}, 6×10^{19} and $1{\cdot}2\times10^{20}$ ev. ml.$^{-1}$ respectively. Decomposition is complete after a total dose of about 2×10^{20} ev. ml.$^{-1}$. Up to about 6×10^{18} ev. ml.$^{-1}$, nitrogen and nitrogen dioxide are the only products observed and the yields of these vary approximately linearly with dose. At greater doses nitrous oxide is formed and, after all of the nitric oxide has disappeared, oxygen is produced. In the interpretation of these results it was assumed that primary ionization leads to the free radical species N and O. Interactions of these atoms with nitric oxide and with the primary reaction products accounts for the observed features of the reaction.[48]

The decomposition of nitric oxide induced by γ-rays and electrons has been studied by Dmitriev *et al.*[49, 50] The effects of pressure, temperature and radiation intensity on the process were investigated, but comparison of the results with those of Harteck and Dondes[48] suggests that the total doses used (i.e., $>2\times10^{19}$ ev. ml.$^{-1}$) were too large to provide information about the initial reaction. At 1 atm. and 20°C., $G(-NO)$ was 14·8, and the products were formed in the ratio $NO_2:N_2:N_2O = 1:0{\cdot}53:0{\cdot}06$. $G(-NO)$ increased by 4% over the pressure range 10 mm.–1·5 atm. and by 10% over the temperature range 0–400°C. Increasing the radiation intensity from 10^{14} to 10^{17} ev. ml.$^{-1}$ sec.$^{-1}$ decreased $G(NO)$ by 30%.

Nitric oxide has been used as a scavenger for free-radicals produced by the irradiation of hydrocarbons.[51, 52]

(c) Nitrogen Dioxide

ELECTRON IMPACT STUDIES

Values of 9·78 ev. and 9·91 ev. obtained for the first ionization potential of nitrogen dioxide by a photo-ionization method[53] and from the dissociation of CH_3NO_2[54] respectively are in agreement, but lower than the value of 13·98 ± 0·12 ev. obtained by direct electron impact. The last value is believed to correspond[55] to a higher electronic state of NO_2^+. If less energetic transitions occur on electron impact, they do so with much smaller cross sections and have not as yet been observed.

Negative ion formation in nitrogen dioxide has been studied as a function of electron energy.[56] The principal ion formed is O^- which appears at $1{\cdot}35 \pm 0{\cdot}05$ ev. From this observation, and the electron affinity of O (1·47 ev.) it was calculated that the maximum value for the dissociation energy of nitrogen dioxide is 2·82 ev.; the value would be lower if the fragments were formed with kinetic energy. NO_2^- ion formation depends on the electron energy in the same way as O^- formation, but the cross-section is smaller than that of the dissociation process by a factor of about 100.[56]

RADIATION-INDUCED DECOMPOSITION

On irradiation of nitrogen dioxide at 550 mm. (70°C.) with ^{235}U fission fragments (dose-rate $= 6{\cdot}0 \times 10^{17}$ ev. ml.$^{-1}$ min.$^{-1}$), Harteck and Dondes[48] found the extent of decomposition to be small ($G(-NO_2) = 0{\cdot}5$) up to a total dose of 6×10^{19} ev. ml.$^{-1}$. At greater total doses, an increased decomposition yield is observed. The products are nitrogen, oxygen and nitrous oxide. The primary processes are believed to lead to the formation of nitric oxide and N and O atoms. Reactions among these three products result largely in the regeneration of nitrogen dioxide and only to a smaller extent in the formation of nitrogen and nitrous oxide. The enhanced decomposition, observed at higher doses, is attributed to the increased absorption of radiation by, and therefore increased decomposition of, the accumulated nitrogen and nitrous oxide.

Dmitriev and Saradzhev,[49, 50] using ^{60}Co γ-radiation to irradiate nitrogen dioxide at 1 atmosphere, obtained $G(-NO_2) = 2{\cdot}1$ and the products $O_2{:}N_2O{:}N_2 = 1{:}0{\cdot}33{:}0{\cdot}25$. The smallest dose used, however, was about 2×10^{19} ev. ml.$^{-1}$ and was, therefore, in the region where Harteck and Dondes[48] found an increased rate of decomposition owing to the primary products taking part in the reaction. The effects of temperature, pressure and dose-rate on the decomposition were also investigated.[50]

(d) Nitrous Oxide

ELECTRON IMPACT STUDIES

Values close to 13·0 ev. have been obtained for the first ionization potential of nitrous oxide by several different methods.[55, 57, 58] The appearance potential of the NO^+ ion from nitrous oxide is not known with certainty, but the most probable value of $15{\cdot}3 \pm 0{\cdot}5$ ev.[55, 57] is about 1 ev. in excess of that calculated from thermochemical data for the process: $N_2O + e \rightarrow NO^+ + N + 2e$, which suggests that excess energy is involved in dissociation by impact. The appearance potential of O^+ was found to be $15{\cdot}33 \pm 0{\cdot}02$ ev.[55]; the close correspondence of the NN–O bond in N_2O, calculated from this, with that from thermochemical data suggests that the process: $N_2O + e \rightarrow N_2 + O^+ + 2e$ occurs with zero excitation and kinetic energy.[55]

Both NO^- and O^- from nitrous oxide have been detected in the mass spectrometer.[46] A ratio NO^-/O^- equal to 1/1000 is found using 25 ev. electrons and a source pressure of 10^{-6} mm. $^{15}N^{14}NO$ and $^{14}N^{15}NO$ give ions of m/e of 30 and 31 respectively, which suggests that NO^- ions are formed almost exclusively (i.e., about 98%) by N–N bond cleavage, probably as a result of dissociation resonance capture.

RADIATION-INDUCED DECOMPOSITION

Early investigations of the decomposition of nitrous oxide, induced by irradiation with electrons[59] and with α-particles,[60–63] left the nature of the products and the reaction mechanism very uncertain. Recent work[64, 65] established that the primary products are nitrogen, oxygen and nitric oxide. Nitrogen dioxide is also formed but probably as a result of secondary reactions involving nitric oxide and oxygen.[64–68] The mechanism of the decomposition is still in doubt. Studies of the mechanism of the ultra-violet photolysis of nitrous oxide[69–71] give some indication of the complexity of the possible reactions of excited and free-radical species in the radiolysis and, in addition, ionic reactions are also presumably involved in the latter.

Essex[72] developed the technique of using an external D.C. field, applied during irradiation, to obtain information about the ionic reactions involved and applied this to the α-particle radiolysis of nitrous oxide.[62, 63] A more detailed investigation using 70 kv. X-rays was made by Burtt and Kircher.[64] The reaction products were determined at different nitrous oxide pressures and field-strengths. At 550 mm. and 200 mm., applied fields up to $X/P=1$ ($X/P=$volts per cm./gas pressure (mm.)) have no effect on the yields of nitrogen, oxygen or nitric oxide, indicating that ion-neutralization processes lead to the same products whether they occur on the electrodes or in the gas phase. At fields between $X/P=1$ and 5 an increase in decomposition to nitrogen and oxygen is observed. Since the ionization-current remains constant over this range of applied voltage, the increase in the decomposition is not due to ionization by collision and is attributed to processes of the following type:

$$N_2O+e^- \rightarrow N_2+O^-$$
$$N_2O+e^- \rightarrow N_2+O+e^-$$
$$N_2O+e^- \rightarrow N+NO+e^-$$
$$N_2O+e^- \rightarrow N+NO^-$$

As the field-strength is increased, the probability per collision of splitting N_2O increases until eventually all of the electrons are attached before reaching the electrode. This point is apparently reached at a field-strength of about $X/P=5$ since further increase in the field-strength does not increase the extent of decomposition. Ultimately, above $X/P=7$, an increase in both the yield and the ionization-current shows that ionization by collision is taking place.

Of considerable interest is the finding that the decomposition yield per unit dose is higher at a pressure of 50 mm. than at 200 mm., an effect which was shown not to be due to a change in the dose-rate. The yield at 50 mm., unlike that at 200 mm., decreases markedly when a small external field is applied. This observation suggests that the increased decomposition at the lower pressure is, to some extent, the result of the neutralization processes and it was estimated that the extent of decomposition attributable to ion-recombination is 30%, 20% and 0% at pressures of 50 mm., 100 mm., and 200 mm. respectively. It was also established that oxygen is not a product of the recombination process.

The use of nitrous oxide as a chemical dosimeter for gaseous systems was recommended by Harteck and Dondes[66] who found the yields of the products to be the same for different types of radiation (pile radiation, fission fragments, and ^{60}Co γ-rays) and to be independent of the gas temperature (25–150°C.) and dose-rate. As a dosimeter this system has many advantages, but unfortunately the absolute yields of the products have not been established with certainty. For comparison of the dose delivered to nitrous oxide, Harteck and Dondes[66] recommend measurement of the sum of nitrogen and oxygen after trapping the unreacted nitrous oxide at liquid nitrogen temperature. However, this method of analysis leads to loss of oxygen by reaction with nitric oxide at the trap temperature.[64] Other workers found it preferable to measure the nitrogen, since the yield of oxygen is influenced by impurities and by reaction with nitric oxide.[65, 73] Values reported for $G(N_2)$ were 11·8 (for 70 kv. X-rays[64]), $11{\cdot}0 \pm 0{\cdot}4$ (for ^{60}Co γ-rays, 4 Mev. X-rays and tritium β-particles[65]) and $12{\cdot}8 \pm 0{\cdot}4$ (for ^{60}Co γ-rays[73]). The yield of nitrogen was linear with dose only up to a total dose of about 10^{17} ev. ml.$^{-1}$ (N_2O at 1 atm. and 20°C.[65, 73]). Colorimetric measurement of nitrite ion, which is formed when irradiated nitrous oxide is extracted with sodium hydroxide solution, has also been used.[74]

(e) Ammonia

ELECTRON IMPACT STUDIES

In the mass spectrum of ammonia the ions NH_3^+, NH_2^+, NH^+, N^+, H^+, NH_3^{++}, NH_2^-, H^- have been observed and the appearance potentials measured.[75]

McDowell[76–78] has discussed the ionization and dissociation of ammonia under electron impact and has designated the electronic states of the ions produced.

An examination of the effect of pressure on the peak heights of the ions in the mass-spectrum[78] shows that the ion-molecule reaction: $NH_3^+ + NH_3 = NH_4^+ + NH_2$ occurs with a rate constant of approximately $0{\cdot}5 \times 10^{-9}$ cm.^{3} molecule^{-1} sec.,$^{-1}$ thus confirming an earlier speculation.[79] No ions containing two nitrogen atoms were detected.

RADIATION-INDUCED DECOMPOSITION

In early studies of the radiolysis of ammonia, values of $G(-NH_3) = 2{\cdot}4$ (18°C.), 9·2 (220°C.) and 10·0 (315°C.) were reported for Rn α-particles[80] and $G(-NH_3) = 3{\cdot}0$ for *X*-rays.[81] In other investigations, the radiolysis of ND_3,[82] the effect of radiation intensity[83, 84] and the effect of the wall material[84] were studied.

Essex and collaborators[85] demonstrated that nitrogen and hydrogen are formed in stoicheiometric proportions in the radiolysis of ammonia and the effects of applied fields were examined. More recently, Dollé[67, 86] showed that nitrogen and hydrogen are the only products when ammonia is irradiated in a reactor; there is no appreciable formation of hydrazine. Using ^{60}Co γ-radiation, Dollé found that the extent of ammonia decomposition is directly proportional to the total dose and $G(-NH_3) = 3{\cdot}27$.

Butt *et al.*,[87, 88] following the work of Essex,[85] studied the radiolysis of ammonia, measuring the yields of nitrogen and hydrogen at different gas pressures and radiation intensities and with applied fields of varying strength. The results were interpreted on the basis of a mechanism derived from an investigation of the photolysis of ammonia.[89] This mechanism involves the NH_2 radical and the H atom as active species:

$$\begin{gathered}
NH_3 \rightarrow NH_3^*\\
NH_3^* \rightleftharpoons NH_2 + H\\
NH_3^* + NH_3 \rightarrow 2NH_3\\
NH_2 + NH_2 \rightarrow N_2H_4\\
2H \rightarrow H_2\\
H + N_2H_4 \rightarrow H_2 + N_2H_3\\
H + N_2H_3 \rightarrow H_2 + N_2H_2\\
N_2H_2 \rightarrow N_2 + H_2
\end{gathered}$$

Photolysis under static conditions gives only nitrogen and hydrogen as products but, in flow experiments, the intermediate hydrazine is found.[89] Burtt did not identify hydrazine as a radiation product. In the radiolysis, it is found that the yield per ion pair decreases with increasing dose-rate and, at low dose-rates, is inversely proportional to the gas pressure. The effect of pressure, as in the case of the photolysis, is believed to be a result of the deactivation process $NH_3^* + NH_3 \rightarrow 2NH_3$. The dose-rate effect is explained in terms of a competition between reactions of $NH_2\cdot$ in the gas-phase and the diffusion of $NH_2\cdot$ to the wall. Ionic reactions are considered to be of little importance since the ion-molecule reactions:

$$\begin{gathered}
NH_2^+ + NH_3 \rightarrow NH_3^+ + NH_2\\
NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2
\end{gathered}$$

would occur and the resulting NH_4^+ would be neutralized at the vessel wall without decomposition.

The above mechanism for the radiolytic reaction must be regarded as somewhat speculative on the basis of the information so far available. An investigation of the initial yields of the different products and a search for hydrazine at low ammonia conversions would be of interest. Hydrazine and nitrogen are formed when ammonia is decomposed in a D.C. electric discharge.[90–92] The hydrazine yield is limited by back-reactions, which to some extent involve atomic hydrogen[92]; maximum yields were $G(N_2) \sim 0{\cdot}8$ and initial $G(N_2H_4) \sim 2{\cdot}5$. Devins and Burton[92] conclude that the primary chemical effects involve only relatively low excited states of ammonia, with energies well below the ionization potential and probably below optically obtainable levels.

(f) **Cyanogen**

ELECTRON IMPACT STUDIES

The ionization and dissociation of cyanogen in the mass-spectrometer have been the subject of several investigations.[93–97] The earlier work has been discussed by McDowell and Warren,[96] who found the appearance potential of C_2N_2 to be 13·57 ev. CN^- ions were found by a resonance capture process at 4·4 ± 0·2 ev. CN^+ was formed with excess of kinetic energy by the process: $C_2N_2 + e \rightarrow CN^+ + CN + 2e$ (appearance potential = 20·4 ev.). The excess energy of the CN ion is found to be 0·57 ev.[97]

By the use of ionization-chamber pressures up to 1 mm. in a mass-spectrometer, transient polymer species from cyanogen have been observed.[98] Peaks corresponding to positive ions from CN^+ to $(CN)_{10}{}^+$ and to negative ions from CN^- to $(CN)_{10}{}^-$ are found. When mixtures of xenon and cyanogen are present in the ionization chamber, the intensity of the negative ions is markedly increased, an effect which is attributed to (*a*) ionization by electrons from xenon, and (*b*) a reaction of a metastable excited xenon ($5p^5\,6s$) with cyanogen to form $CN\cdot$ radicals which are subsequently ionized. An addition complex $[Xe(CN)_2]^+$ postulated by Eyring[99] is also observed.

RADIATION-INDUCED POLYMERIZATION, OXIDATION AND REDUCTION

Lind and Bardwell[100] found that irradiation of cyanogen with radon α-particles induces polymerization to a black solid material. Experiments in which cyanogen was irradiated in the presence of xenon show that the polymerization can be initiated by energy absorbed by the xenon. Eyring[99] suggests that addition of Xe^+ to cyanogen is a probable initiation step, a theory which receives support from recent mass-spectrometric studies[98] (see above).

Irradiation of cyanogen–oxygen mixtures with α-particles gives a yellow solid polymerized addition product, $(CNO)_x$, together with carbon dioxide, carbon monoxide and nitrogen.[100] The reaction mechanism has not been investigated.

α-Radiolysis of cyanogen–hydrogen mixtures is believed to result in a hydrogenated polymer, since both cyanogen and hydrogen are consumed[100] but a detailed study of the process has not been carried out.

(g) **Hydrazine**

ELECTRON IMPACT STUDIES

The relative abundances and appearance potentials of the principal ions in the mass-spectrum of hydrazine and the several methyl substituted hydrazines have been measured.[101] The ions from hydrazine and their appearance potentials are: $N_2H_4{}^+$ (9·0 ev.), $N_2H_3{}^+$ (11·3 ev.), $N_2H_2{}^+$ (11·9, 16·6 ev.), N_2H^+ (14·8 ev.), $N_2{}^+$ (16·2 ev.).

RADIATION-INDUCED DECOMPOSITION

The decomposition of hydrazine at 10 mm. and 20°C. induced by α-rays has been reported[102] to occur with a yield corresponding to $G(-N_2H_4) = 11{\cdot}1$ and an overall stoicheiometry: $2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2$. The intermediate reaction steps were not investigated. Some of the species which might be involved are suggested by a study of the products formed when hydrazine is subjected to an electric discharge.[103] Examination of the species in the discharge, by means of a mass-spectrometer designed to detect free-radicals, shows the presence of di-imide N_2H_2, triazene N_3H_3, and tetrazene N_4H_4, and the free-radicals N_2H_3 and NH_2. The ionization potentials of these species were also determined.

LIQUID AMMONIA

Roberts and Allen[104] found that no change in electrical conductivity occurs in liquid ammonia either during or after irradiation with 2 Mev. electrons or 2 Mev. X-rays and concluded that stable trapped electrons are not formed.

A detailed study of the radiation chemistry of liquid ammonia has been carried out by Cleaver, Collinson and Dainton[105] using ^{60}Co γ-rays and 50 kv. X-rays. The yields of the products from pure ammonia and the effects of various scavengers were interpreted on the assumption that both free-radical species, NH_2 and H, and molecular species, hydrazine and hydrogen, are formed in the primary decomposition. The yields were $G_{NH_2} = G_{H_2} = 1{\cdot}75$ and $G_{H_2} = G_{N_2N_4} = 0{\cdot}125$.

From pure ammonia the products are hydrogen, nitrogen and hydrazine. The initial yields are directly proportional to the dose and are: $G(H_2) = 0{\cdot}81 \pm 0{\cdot}03$, $G(N_2) = 0{\cdot}22 \pm 0{\cdot}07$ and $G(N_2H_4) = 0{\cdot}13 \pm 0{\cdot}3$. These products are formed partly as molecular products and partly as a net result of the various possible recombination reactions of the free radicals.

The disappearance of the blue colour from solutions of sodium in liquid ammonia, which occurs on irradiation, is attributed to reaction of the radical NH_2 with the solvated electrons present in sodium solution. Spectrophotometric measurement of the colour disappearance gave the value for $G_{NH_2} = 1{\cdot}75$. The yield of hydrazine in sodium solutions was $G_{N_2H_4} = 0{\cdot}125$. A quinone dye, formed in liquid ammonia solution from methylene blue, is effective as a scavenger for H and NH_2. The rate of disappearance of the dye gave a value for $G_H + G_{NH_2} = 3{\cdot}5$. The hydrogen yield with this scavenger was $G_{H_2} = 0{\cdot}125$.

The product yields from ammonia solutions of 0·1 M. ammonium chloride ('acidic solution') or 0·1 M. potassium chloride ('neutral solution') are the same as from pure ammonia. In 0·1 M. sodamide ('basic') solutions, however, the yields are less than from pure ammonia: $G(H_2) = 0{\cdot}14 \pm 0{\cdot}02$, $G(N_2) = 0{\cdot}13 \pm 0{\cdot}01$ and $G(N_2H_4) = 0{\cdot}005$. This decrease is attributed to the processes:

$$H + NH_2^- \rightleftharpoons NH_3^- \; (\equiv e^- \text{ amm.})$$
$$NH_3^- + NH_2 \rightleftharpoons NH_2^- + NH_3$$

the net effect of which is an enhancement of the recombination:

$$H + NH_2 \rightarrow NH_3$$

The origins of the primary species H, NH_2, N_2H_4, and H_2 were discussed in terms of the radiation-induced excitation and ionization processes. It was concluded that a reasonable quantitative picture could be given of the decomposition of liquid ammonia if it were assumed that the fate of the secondary electrons is charge-neutralization of either the primary NH_3^+ ion or the ions produced by ion-molecule reactions such as: $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$. The primary processes in liquid ammonia were compared with those in water.

AQUEOUS SOLUTIONS

A detailed account of the radiation chemistry of water and aqueous solutions is given in a monograph by Allen[106] and only a brief outline of the features relevant to the following section on aqueous solutions of nitrogen compounds will be given here.

In dilute aqueous solution, the reactions which occur on irradiation are a result of the absorption of radiation by the water. The chemical effects of this absorption can, in general, be interpreted in terms of the formation of free radicals[107] and molecular products[108]:

$$H_2O \rightsquigarrow H, OH, H_2, H_2O_2$$

the stoicheiometry of the process being represented by:

$$G_{-H_2O} = 2G_H + G_{H_2} = 2G_{OH} + G_{H_2O_2}$$

where G_H, G_{OH}, G_{H_2}, $G_{H_2O_2}$ are the G-values for the formation of the species from water. The formation of the molecular products is, to some extent at least, a consequence of the non-uniform distribution of primary events, which results in the occurrence of reactions such as $H + H \rightarrow H_2$, $OH + OH \rightarrow H_2O_2$, in regions of high radical density ('spurs') along the ionizing particle track. Since the distribution of primary events depends on the linear energy transfer (LET) of the radiation,[106] the values of G_H, G_{OH}, G_{H_2}, $G_{H_2O_2}$ depend on the type of radiation used. The values are also a function of the pH of the irradiated solution.[106] Furthermore, there is evidence that the forms of the free-radical species, represented above as H and OH, are dependent on the pH. At high pH, the dissociation of OH ($OH \rightleftharpoons O^- + H^+$) occurs.[109] Also, the species first considered to be the H-atom may actually represent more than one different species, which may be distinguished in certain circumstances. It was first suggested by Weiss[110, 111] that H_2^+, formed by the process: $H + H^+ \rightarrow H_2^+$, could play a rôle in the radiation chemistry of aqueous solutions. Barr and Allen[112] found that the 'H-atom' produced by the process $OH + H_2 \rightarrow H + H_2O$ differs from that formed by the radiolysis of water. Allan and Scholes[113] demonstrated the presence of two forms of 'H-atom' in irradiated water. It was suggested that these two species are the H-atom and the electron; the latter could react thus: $e_{aq} + H^+ \rightarrow H^{\cdot}$, a process which occurs in competition with other reactions of the electron and therefore becomes important as the pH is decreased. Weiss[114] discussed the nature of the electron in water and concluded that it must be similar to a self-trapped electron ('polaron') in a crystalline solid and should have a sufficiently long lifetime to be important as an active entity in irradiated water.

When pure water is irradiated, the free radicals either undergo recombination reactions or react with the molecular products. A solute capable of reacting with the free radicals may successfully compete with the radical recombination reactions and, when its concentration is sufficiently high, may scavenge all of the radicals present. At high concentrations a solute may also compete successfully with the recombination processes, occurring in the 'spurs', which are responsible for the molecular products H_2 and H_2O_2. This has the effect of increasing G_H and G_{OH} at the expense of G_{H_2} and $G_{H_2O_2}$. Direct effects, *i.e.*, solute decomposition due to primary absorption of the radiation by the solute, can also become of importance as the solute concentration is increased.

(a) **Nitrate Ions**

Several early investigations showed that nitrite and oxygen are formed as a result of irradiating nitrate solutions.[115, 116] Some of the effects of pH on the yields have been investigated.[117, 118]

The mechanism of the radiation-induced decomposition in dilute aqueous solution has not been fully established. From a study of the action of pile-radiation (fast neutron-γ) on calcium nitrate solutions, Sowden[119] suggested the following mechanism:

$$NO_3^- + H \rightarrow NO_2 + OH^-$$

$$2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+$$

$$NO_2^- + OH \rightarrow NO_2 + OH^-$$

$$NO_2^- + H_2O_2 \rightarrow NO_3^- + H_2O$$

Refs. p. 559

The extent to which direct action plays a part is an interesting feature of the radiation chemistry of nitrate solutions. The G-value for the reduction of ceric to cerous salt was found to be increased when nitrate ions are present.[120] This increase was found by Sworski[121] to be due to a direct effect, involving primary absorption of the radiation by the nitrate ions; this direct effect has been studied by Mahlman and co-workers[122] who measured the formation of cerous from ceric salt in the presence of nitrate. In the absence of nitrate the cerous yield was given by $G(Ce^{3+}) = G_H + 2G_{H_2O_2} - G_{OH}$. Any nitrite formed by direct action reduced ceric salt according to the reaction: $NO_2^- + 2Ce^{4+} + H_2O \rightarrow 2Ce^{3+} + 2H^+ + NO_3^-$, thus giving an increased cerous yield. This increase in the yield of cerous salt as the nitrate concentration is increased therefore gives a measure of the direct effect.[122] The nitrite produced by direct action is independent of the cation present (Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Zn^{++}, Mg^{++}, Al^{+++} and Tl^+), and can be represented by the equation: $G(NO_2^-)_{DA} = 1{\cdot}22 \log [NO_3^-] + 1{\cdot}70$, where $G(NO_2^-)_{DA}$ is the formation of nitrite by direct action and $[NO_3^-]$ is the nitrate molarity. The direct decomposition of the nitrate ion is believed to involve the process: $NO_3^- \rightsquigarrow NO_2^- + \frac{1}{2}O_2$. In nitric acid solutions[123] there is evidence that the direct effect involves two different processes:

$$HNO_3 \rightsquigarrow HNO_3^* \rightarrow OH + NO_2 \qquad \text{('radical')}$$

$$HNO_3 \rightsquigarrow HNO_3^* \rightarrow HNO_2 + \tfrac{1}{2}O_2 \qquad \text{('molecular')}$$

Thus, in nitric acid solutions, G_{OH} increased linearly with the nitric acid concentration, the direct 'radical' process increasing from $G = 0$ at zero HNO_3 to $G = 1{\cdot}89$ at 7·0 M. HNO_3.

Changes in $G(H_2)$ with nitrate concentration are of interest because of their bearing on the mechanism of formation of molecular hydrogen in irradiated water. Mahlman[124] showed that $G(H_2)$ from sodium nitrate solutions irradiated with ^{60}Co γ-rays is directly proportional to the cube root of the nitrate activity, up to a concentration of 1·0 M. sodium nitrate, obeying the relationship: $G(H_2) = -0{\cdot}46[\gamma\ NaNO_3]^{1/3} + 0{\cdot}46$ where $[\gamma\ NaNO_3]$ was the activity calculated using experimentally determined activity coefficients. A plot of $G(H_2)$ against $[\gamma\ NaNO_3]$ shows a sharp break at a concentration of about 1·3 M.[126] and it is concluded that there are two different mechanisms for the formation of molecular hydrogen in irradiated water. A comparison of the dependence of $G(H_2)$ on nitrate concentration for different types of radiation (^{60}Co γ-rays, fast neutron-γ-rays, and fission fragments) has been made by Sowden.[119]

(b) Nitrite Ions

The effect of X-rays on dilute solutions of potassium nitrite was first investigated by Fricke and Hart.[127] A detailed study of the radiation chemistry of de-aerated solutions of nitrite was made by Schwartz and Allen[128] and Schwartz and Salzman.[129] The initial products are hydrogen and hydrogen peroxide, nitrate appearing only after some hydrogen peroxide has accumulated. The proposed mechanism is[128]:

$$OH + NO_2^- \rightarrow OH^- + NO_2$$

$$H + NO_2^- \rightarrow NO + OH^-$$

$$H + H_2O_2 \rightarrow H_2O + OH$$

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

$$2NO_2 + H_2O \rightarrow HNO_2 + H^+ + NO_3^-$$

Reaction of hydrogen atoms with nitrate: $H + NO_3^- \rightarrow NO_2 + OH^-$, has also to be taken into consideration at the higher doses used.[129] It was found that H atoms react with hydrogen peroxide and nitrate at about equal rates; the reaction with nitrite is slower by a factor of about two. The reaction in the presence of dissolved oxygen has not been completely elucidated.

(c) Azide Ions

In an investigation of the radiation chemistry of azide ion, Kelly and Smith[130] found the products from de-aerated sodium azide solutions (pH 8) irradiated with 200 kv. *X*-rays to be nitrogen, ammonia, nitrite and nitrous oxide. The initial yields increased with increasing azide concentration and were measured over the concentration range 10^{-3} to 1·0 M. azide. At 10^{-3} M. azide, the initial yields were: $G(-N_3)=3{\cdot}1$, $G(NH_3)=0{\cdot}65$, $G(N_2)=4{\cdot}4$, $G(H_2)=0{\cdot}7$, $G(NO_2^-)\sim 0{\cdot}02$ and $G(N_2O)\sim 0{\cdot}003$. At 1·0 M. azide, the values obtained were: $G(N_2)=12{\cdot}5$, $G(NH_3)=2{\cdot}9$, $G(H_2)=0{\cdot}5$, $G(N_2O)=0{\cdot}4$.

In oxygenated solution (10^{-3} M. azide), the extent of azide decomposition ($G(-N_3^-)=0{\cdot}9\pm 0{\cdot}1$) is markedly less than in the absence of oxygen. Hydrogen peroxide ($G(H_2O_2)=0{\cdot}9\pm 0{\cdot}1$) is the only product detectable in solution; the gaseous products were not fully investigated under these conditions but nitrous oxide was formed ($G(N_2O)=0{\cdot}2$).

When hydrogen peroxide (10^{-4} M.) is present, irradiation of 10^{-1} M. azide gives a lower yield of nitrogen ($G(N_2)=5{\cdot}4$) and ammonia ($G(NH_3)=0{\cdot}8$), but an increased yield of nitrous oxide ($G(N_2O)=0{\cdot}6$) and oxygen ($G(O_2)=0{\cdot}54$). Similar results were obtained for other azide concentrations.

A mechanism was proposed in which the H-atom (or solvated electron) and OH-radical react with azide:

$$\text{H (or } e_{\text{H}_2\text{O}}^-) + N_3^- \rightarrow NH^- + N_2$$
$$NH^- + H_2O \rightarrow NH_2 + OH^-$$
$$OH + N_3^- \rightarrow N_3 + OH^-$$

At low azide concentrations, the labile species formed in these reactions undergoes interaction to give the observed products, e.g.:

$$H + N_3 \rightarrow N_3^- + H^+$$
$$2N_3 \rightarrow 3N_2$$
$$NH_2 + H \rightarrow NH_3$$

At higher concentrations the reactions:

$$NH_2 + N_3^- \rightarrow NH_2^- + N_3$$
$$NH_2^- + H_2O \rightarrow NH_3 + OH^-$$

become increasingly important, leading to increased azide decomposition. The molecular hydrogen peroxide is consumed in the reaction:

$$N_3 + H_2O_2 \rightarrow N_2 + NOH + OH$$

which leads to nitrous oxide formation: $2NOH \rightarrow N_2O + H_2O$.

In oxygenated solution the markedly lowered extent of azide decomposition is attributed to the back-reaction: $N_3 + O_2^- \rightarrow N_3^- + O_2$, where O_2^- arises from the reaction: $H + O_2 \rightleftharpoons H^+ + O_2^-$.

Irradiation of azide solutions containing other solutes (methanol, *iso*propanol, acetone and formaldehyde) gives results which are interpreted using the mechanism outlined above together with the concept[113] that two types of 'H-atom' are formed when water is irradiated.

(d) Ammonia

Rigg, Scholes and Weiss[131] found that nitrite is formed when oxygenated solutions of ammonia are irradiated (200 kv. *X*-rays). The yield of nitrite is markedly dependent on the pH, the oxidation only occurring when the pH is sufficiently high for free ammonia to be present. It was shown that hydroxylamine is not a product or an intermediate in the oxidation and it was suggested that the mechanism might involve the NH_2 radical formed in reaction: $NH_3+OH \rightarrow NH_2+H_2O$. The NH_2 possibly reacts with molecular oxygen, $NH_2+O_2 \rightarrow NH_2O_2$, to give a radical which, on oxidation, gives nitrous acid. Alternatively, disproportionation, $2NH_2 \rightarrow NH+NH_3$, possibly occurs giving the imine radical, NH, which would react with molecular oxygen to give nitrous acid: $NH+O_2 \rightarrow HNO_2$. In de-aerated solutions, neither nitrite, hydroxylamine, nor hydrazine could be detected as products.

(e) Hydrazine

The decomposition of hydrazine in aqueous solution, induced by ^{60}Co γ-radiation, has been studied by Dewhurst and Burton[132] and by Lefort and Haissinsky.[133] In de-aerated solution, nitrogen, hydrogen, and ammonia are the only products, the stoicheiometry of the decomposition being represented by: $2N_2H_4 \rightarrow 2NH_3+H_2+N_2$. The yield of the products increases with increasing hydrazine concentration until this is about 2×10^{-2} M., after which it remains constant up to the highest concentrations used. The yields are constant over the pH range 0·5 to 8·0 but decrease when the pH exceeds 8·0. At pH 2·0, and in the concentration independent region, $G(-N_2H_4)=G(NH_3)=5{\cdot}1$, $G(H_2)=G(N_2)=2{\cdot}4$.[132] These results suggest that both H and OH react with hydrazine:

$$H+N_2H_4 \rightarrow H_2+N_2H_3$$

$$OH+N_2H_4 \rightarrow H_2O+N_2H_3$$

$$2N_2H_3 \rightarrow N_2+2NH_3$$

However, to account for the absence of hydrogen peroxide as a product, it must also be assumed that the molecular hydrogen peroxide is decomposed, presumably by reaction with H-atoms: $H+H_2O_2 \rightarrow OH+H_2O$. Inclusion of this reaction would be consistent with the observed $G(H_2)=2{\cdot}5$ and the observation that addition of low concentrations of hydrogen peroxide ($<10^{-3}$ M.) to the solution prior to irradiation lowers $G(H_2)$ but does not influence the values of $G(NH_3)$ and $G(N_2)$. In the presence of concentrations of hydrogen peroxide greater than 10^{-3} M., the nitrogen yield remains unchanged but the ammonia yield decreases; e.g., $G(NH_3)=1{\cdot}0$ with 10^{-2} M. hydrogen peroxide present (2×10^{-2} M. hydrazine). This suggests that hydrogen peroxide reacts with the intermediate radicals involved in the hydrazine decomposition. Dewhurst and Burton[132] suggested that the long-lived intermediate N_4H_6 is formed by the reaction: $2N_2H_3 \rightarrow N_4H_6$. In the absence of hydrogen peroxide this decomposes: $N_4H_6 \rightarrow N_2+2NH_3$, while in the presence of hydrogen peroxide the reaction: $N_4H_6+H_2O_2 \rightarrow N_2+N_2H_4+2H_2O$ takes place. Lefort and Haissinsky[133] found that in oxygenated solutions, nitrogen is the only product. Thus the reactions in the presence of oxygen appear to be similar to those in the presence of hydrogen peroxide. From hydrazine solutions irradiated with Po α-rays, the chief products are hydrogen, oxygen and hydrogen peroxide, the hydrazine decomposition being small, owing to the relatively small free-radical yield obtained with this type of radiation.

(f) Hydroxylamine

De-aerated solutions of hydroxylamine (pH 4), irradiated with ^{60}Co γ-rays gave the following yields[134, 135]: $G(-NH_2OH)=6{\cdot}8$, $G(NH_3)=2{\cdot}25$, $G(N_2)=2{\cdot}0$, $G(N_2O)=0{\cdot}33$, $G(H_2)=0{\cdot}45$. The decomposition process is dependent on the pH of the solution, the production of nitrous oxide being negligible at pH 6. The production of ammonia is low at pH 2, increases in the pH region 2–6, and remains constant ($G(NH_3)=2{\cdot}7$) at pH 6. The product yields decrease with decreasing dose. In the presence of air, the yield of ammonia is lower and the yield of nitrate higher than in de-aerated solution. The kinetics of the decomposition of hydroxylamine have been discussed.[136]

(g) Nitrous Oxide

The radiation chemistry of nitrous oxide in aqueous solution has been investigated by Dainton and co-workers.[137, 138] They were unable to confirm the finding of Soviet workers[139] that the yield of Fe^{3+} from Fe^{2+} solutions is greater in solutions saturated with nitrous oxide than in de-aerated solutions. The results of Dainton show that OH radicals do not react with nitrous oxide. The nitrogen yields at $pH > 2{\cdot}7$ are those expected if all of the available H-atoms, or their stoicheiometric equivalents, react with nitrous oxide according to: $H + N_2O \rightarrow N_2 + OH$. At $pH < 2{\cdot}7$ $G(N_2)$ decreases with decreasing pH. The decrease is attributed to the formation of H_2^+, which is incapable of reacting with nitrous oxide. $G(N_2)$ does not become zero at the lowest pH studied, a result which is explained by the assumption that different species of H-atom, or H-atom precursor, are formed in irradiated water.

SOLID SYSTEMS

The basic processes which occur when a solid is irradiated have been discussed in detail elsewhere.[140, 141] In the case of heavy particle and fission-fragment irradiation some part is played by atomic displacement but with the sources commonly used for radiation-chemical studies (*X*-rays, γ-rays, and electrons below about 5 Mev.) the important processes, in the type of crystalline solid we are concerned with here, are ionization and electronic excitation. The electrons, positive holes, and excitons produced are mobile to some extent and trapping may occur at lattice defects or other imperfections. Decomposition may follow excitation or may occur as a result of recombination of electrons and holes.

Information about the chemical effects of radiation in solids can be obtained from physical measurements, such as microwave resonance absorption and light absorption. Chemical investigations may involve determination of gaseous products and of the products formed when the irradiated solid is taken into solution. A combination of such techniques is often necessary.

(a) Nitrates

Solid anhydrous nitrates, when irradiated with *X*-rays, fast electrons or pile radiation, decompose to give nitrite and oxygen.[142, 143] Nitrite has been detected in irradiated sodium nitrate crystals by means of its ultra-violet absorption spectrum[144] and also, chemically, in solutions of various irradiated nitrates.[142, 143] Oxygen has been detected after liberation from the irradiated crystal by heating or by dissolving in water.[143] The amount of oxygen formed has usually been reported as equivalent to the nitrite, giving decomposition according to: $2NO_3^- \rightarrow 2NO_2^- + O_2$.[145] However, it cannot be assumed that this is necessarily true in all cases. This is demonstrated by the work of Jones and Durfee,[146] who irradiated with ^{60}Co γ-rays nitrate ions dispersed in a potassium bromide lattice. The decomposition of nitrate and formation of nitrite were followed by infra-red measurements on the crystal. For the initial stages of the reaction, $G(NO_2^-) = G(-NO_3^-)$ but although $G(-NO_3^-)$ remains constant up to the highest doses used $G(NO_2^-)$ decreases with increasing dose. This suggests that nitrite is involved in a secondary decomposition process, the products of which were not identified. Also, in the case of lead nitrate,[147] it is found that in the initial stages of the decomposition the yield of nitrite is equal to the yield of oxygen. As the extent of decomposition increases, the oxygen yield falls to a steady value of approximately one-half of the nitrite yield. The explanation advanced to explain these results involves a radiation-induced decomposition: $Pb(NO_3)_2 \rightsquigarrow Pb + 2NO_2 + O_2$ and the secondary reaction: $Pb + \frac{1}{2}O_2 \rightsquigarrow PbO$. Bleaney, Hayes and Llewellyn[148] have obtained evidence that nitrogen dioxide can be formed in irradiated nitrate crystals. The radiation damage in lanthanum magnesium nitrate crystals ($La_2Mg_3(NO_3)_{12}$,$24H_2O$) caused by growing these in solutions containing ^{241}Am (5·5 Mev. α-particles) or ^{147}Pr (0·22 Mev. β-particles) or subjecting the crystal to ^{60}Co γ-radiation, was investigated by means of the paramagnetic resonance spectrum. The presence of nitrogen dioxide was indicated by examination of the hyperfine structure.

Cunningham and Heal[145, 149] investigated the decomposition of the alkali metal nitrates induced by 44·5 kvp. *X*-rays. Kinetic studies were made of the decomposition of potassium nitrate up to high conversions (28·5% decomposition). The yield of nitrite per unit dose is initially constant but falls to a lower value when the extent of decomposition has reached between 1·5 and 2·5%. This lower value remains proportional to the amount of decomposed nitrate up to the highest doses used. The initial yield of nitrite increases with increasing temperature from $G(NO_2^-) = 1{\cdot}81 \pm 0{\cdot}10$ at -186°C. to $G(NO_2^-) = 3{\cdot}34 \pm 0{\cdot}10$ at 200°C. The radiation sensitivities of various nitrates were compared by measuring the initial nitrite yields. The following values were obtained for $G(NO_2^-)$, the irradiations being carried out at 15°C. unless otherwise stated: $LiNO_3$ 0·02 ± 0·01 (fused sample), 0·006 ± 0·003 (dehydrated sample); $NaNO_3$ 0·37 ± 0·05, 1·10 ± 0·05 (150°C.); $RbNO_3$ 0·04 ± 0·10, 1·37 ± 0·10 (150°C.); $CsNO_3$ 1·37 ± 0·30, 1·17 ± 0·10 (150°C.); $AgNO_3$ 0·14 ± 0·02; $Ba(NO_3)_2$ 1·75 ± 0·25, 1·84 ± 0·25 (150°C.); $Sr(NO_3)_2$ 0·52 ± 0·05, 1·33 ± 0·05 (150°C.). Samples of potassium nitrate which had been treated differently before irradiation gave the same $G(NO_2^-)$ but samples of lithium nitrate, which differed markedly in their degree of crystalline perfection, gave different values for $G(NO_2^-)$ (see above); the less perfect form gave the lower $G(NO_2^-)$ value. The value of $G(NO_2^-)$ was found to be independent of the dose-rate and it was concluded that the decomposition does not involve interaction of two excited ions or of two NO_3 radicals. Results obtained in studies of the *X*-ray patterns and infra-red spectra, together with the observation that increasing the crystal imperfection does not increase $G(NO_2^-)$, led to the conclusion that special trapping centres, such as crystal imperfections, are not of importance as sites for nitrate ion dissociation.

A correlation between the extent of decomposition per unit dose in different nitrates and the free-space in the crystal lattice (i.e., the difference between the actual volume of the crystal per ion-pair and the combined volume of the ions calculated from standard ionic radii) was first reported by Hennig, Lees and Matheson.[143] Cunningham and Heal[149] also found that $G(NO_2^-)$ increases with increasing free-space in the nitrates they studied. Baberkin[150] compared the yields of nitrate from barium, strontium, calcium, cadmium and zinc nitrates and arrived at similar results. As an explanation of this effect it was suggested[149] that the probability of dissociation is related to the ability of the oxygen atom to move away from the nitrite fragment through the surrounding 'cage' of ions; possibly this movement involves less energy in crystals of large free-space than in crystals where the ions are closely packed.

The observed variation of $G(NO_2^-)$ with temperature was attributed by Cunningham and Heal[149] to the need for thermal activation energy to complete the dissociation and it was suggested that the differences between $G(NO_2^-)$ for different nitrates at different temperatures arise chiefly from the different amounts of thermal activation energy required. Thus low values of $G(NO_2^-)$ are usually associated with correspondingly high temperature coefficients of $G(NO_2^-)$, a fact which is explained by attributing the decomposition to the thermally activated dissociation of a single electronically excited state. The energies of activation for dissociation in sodium, rubidium and strontium nitrates, calculated from the variation of $G(NO_2^-)$ with temperature, are in reasonable agreement with those calculated from the absolute value of $G(NO_2^-)$ at 15°C.

Information about the importance of lattice disturbances in the decomposition processes in irradiated nitrates was obtained by Forten and Johnson.[151, 152] The heats of solution and densities of potassium, cæsium, lead, and sodium nitrates and the yields of nitrite were measured as functions of radiation dose. As found previously,[149] breaks occur in plots of the yield of nitrite against total dose. These breaks coincide with maxima in the heats of solution and with density changes in the irradiated salts. It was concluded that the three phenomena, viz., changes in the nitrite yield, heats of solution and density, are related and probably arise from a transition, resembling a lambda transition, induced when a certain extent of decomposition has taken place.

Maddock and Mohanty[153, 154] investigated the effect of post-irradiation thermal annealing on the formation of nitrite from lead nitrate. For lead nitrate irradiated with 2 Mev. electrons or ^{60}Co γ-rays, it is possible to interpret the annealing results in terms of a combination of a unimolecular and a bimolecular process with activation energies of 13 and 31·5 kcal. respectively. Since annealing in the absence of air gives the same results as when air is present, and heating a synthetic solution of lead nitrite in lead nitrate does not result in nitrite disappearance, it is concluded that the annealing reaction cannot be ascribed to either an atmospheric oxidation or a thermal decomposition of the nitrite. Large and small size crystals behave similarly, which indicates that the decomposition takes place at normal lattice sites.[149] It was suggested that radiolysis leads to NO_2^-, O and NO_2, O^- pairs and that in about 16% of the pairs formed the species are sufficiently close together to require an activation energy of only 13 kcal. for recombination; recombination of these closely adjacent pairs is therefore responsible for the low energy recombination process. In the remaining dissociation events, the oxygen atoms penetrate far enough into the lattice and remain mobile long enough to combine to produce molecular oxygen, which accounts for the second-order annealing process. Comparison of the results obtained from electron and γ-radiation suggests that the extent to which radiolysis produces pairs which combine with low activation energy is related to the fraction of nitrate ions in a particular environment. Thus it appears possible that there is a limiting value for the number of NO_2^- and O pairs, possibly determined by the density of some defects in the crystals, and that, when all of the O traps are filled, subsequent radiolysis leads to oxygen production.

(b) Sodium Nitrite

Livingstone and Zeldes[155] examined the hyperfine electron spin resonance of single crystals of sodium nitrite irradiated at 77°K. with ^{60}Co γ-radiation. A paramagnetic species believed to be NO_2 was formed. The yield of this species is greatly enhanced by incorporation of silver nitrite in the sodium nitrite lattice. This is consistent with the interpretation that NO_2 is stably formed by removal of an electron from NO_2^- since the Ag^+ ion could serve as a trap for the electron, which otherwise would back-react with NO_2 on warming.

(c) Azides

In a study of the decomposition of sodium azide induced by 50 kv. *X*-rays, Heal[156, 157] obtained evidence for the presence of either trapped electrons or sodium atoms by dissolving the irradiated salt in liquid ammonia at −78°C., when a blue colour is produced which is indistinguishable from that of solutions of sodium in liquid ammonia. It was concluded that the net decomposition can be represented:

$$NaN_3 \rightsquigarrow \tfrac{3}{2}N_2 + Na$$

or

$$N_3^- \rightsquigarrow \tfrac{3}{2}N_2 + e^-$$

When the irradiated salt is dissolved in water, nitrogen is evolved and ammonia formed, the yield of nitrogen being approximately four times the yield of ammonia. It is assumed that the nitrogen liberated is that formed in the solid during irradiation and that the ammonia results from reduction of azide ions either by solvated electrons or by hydrogen atoms, produced by reaction of sodium with water, according to the net process: $8e^-(\text{or Na}) + 9H^+ + N_3^- \rightarrow 3NH_3$. (Recent evidence suggests that reduction of azide by H-atoms (or electrons) occurs according to the net reaction:

$$H + 2N_3^- + 2H^+ \rightarrow NH_3 + \tfrac{5}{2}N_2$$

This being so, a primary process as represented by Heal (see above) would give a nitrogen yield four times the ammonia yield, as observed, but the nitrogen yield from the irradiated salt dissolved in water would be equivalent to four times the yield of azide decomposed, i.e., the actual $G(-\mathrm{NaN_3})$ would be three-eighths of that calculated by Heal from nitrogen yields.)

The extent of decomposition of azide, determined by measuring the nitrogen evolved in water, is independent of dose-rate and directly proportional to the total dose up to at least 2% decomposition. The decomposition increases with increasing temperature between −186°C. and +202°C. No thermal decomposition occurs even at the highest temperatures used. The effect of temperature was interpreted in terms of two processes: *A*, the rate of which varies little with temperature and which is responsible for most of the decomposition at low temperatures, and *B*, a temperature-dependent process, effective mainly above room-temperature, which causes most of the decomposition at 200°C. Process *A* was ascribed to positive holes generated directly by irradiation, the N_3 radicals formed being assumed to react with an adjacent N_3^- ion in a process of low activation energy: $N_3+N_3^- \rightarrow 3N_2+e$. Process *B* was attributed to the thermal activation of trapped excitons to give electrons in the conduction band and positive holes, which then react as in process *A*.

Absorption bands, resembling the well-known *F*, *V*, etc. bands of the alkali metal halides, develop in azides when these are exposed to ultra-violet light or *X*-rays. Unlike the bands formed in halides, the bands in irradiated azides are unstable at room temperature and persist only at low temperatures.[158] The absorption bands produced in alkali metal azides by *X*-irradiation have been investigated by Cunningham and Tompkins[159] and by Heal and Pringle.[160] The nature and mechanism of the formation of these absorption centres and the changes observed on increasing the temperature were discussed.

The thermal decomposition and explosion characteristics of irradiated α-lead azide have been investigated.[161–163]

When solid HN_3 at liquid nitrogen temperature is bombarded with ions and electrons produced by means of a Tesla coil discharge, a blue colour is produced which is attributed to the formation of free radicals.[164, 165]

(d) Ammonia

Solid ammonia at liquid nitrogen temperature irradiated with ^{60}Co γ-rays gives an electron spin resonance spectrum which was interpreted as being due to H and NH_2 free radicals.[166] The irradiated solid reveals a complex annealing pattern, the peaks attributed to H and NH_2 disappearing at 100–110°K., but a peak due to the formation of a new and unidentified species at $g=2{\cdot}0$ increased in intensity and finally annealed out at about 140°K.

(e) Hydrazine

The decomposition of hydrazine at −187°C. by the ions and electrons produced in a Tesla coil discharge has been examined.[167] Nitrogen, ammonia and hydrogen are evolved as the solid warms up after bombardment. The absorption spectrum of the treated solid shows the absence of NH_2 radicals. The results indicate the formation of nitrogen compounds such as triazene, which are stabilized at low temperatures and which decompose as the solid warms up.

(f) Ammonium Perchlorate

The thermal decomposition of ammonium perchlorate after irradiation with *X*-rays (50 kv.) and γ-rays (^{60}Co) has been investigated by Freeman, Anderson and Campisi.[168] The loss of weight was measured as a function of temperature as the sample was heated from room temperature to an elevated temperature at a rate of 5°C. per minute. Use was also made of the technique of differential thermal analysis, i.e., the continuous measurement of the temperature difference of the ammonium perchlorate sample and a thermally inert reference compound (powdered alumina) as a function of the time of heating as both the sample and the reference compound were heated at a predetermined rate (5° per minute). In addition the decomposition was studied by microscopic observations.

The results show that several stages of reaction are involved in the thermal decomposition and that the low temperature stages are appreciably enhanced as a result of pre-irradiation. The relative importance of the various stages of reaction is a function of radiation dose. It is suggested that the increased reactivity after irradiation may be due to the presence of positive holes which would favour an electron transfer mechanism of decomposition. The effect of impurities such as Ag^+, Cu^{2+}, and I^-, seems to support this view.

(g) Sodium Cyanide

Sodium cyanide crystals, irradiated with 40 kv. *X*-rays, colour only with difficulty, the intensity of coloration being approximately proportional to the radiation dose.[169] Absorptions are found in the irradiated crystals at 5400, 4570 and 3600 A., together with a general increase in absorption at shorter wave-lengths. The colorations are unstable, bleaching at 30°C. with a half-time of about 27 minutes. At temperatures above 15°C., the orientation of the CN^- ions in the crystal is random, owing to the occurrence of an occasional re-orientation process. It is considered that this occasional re-orientation process facilitates the recombination of electrons and positive holes in the irradiated crystal, leading to bleaching. At 0°C., where the re-orientation process does not occur, the half-time for bleaching is about ten times greater than would have been expected from extrapolation of data from temperatures above the critical disordering temperature.

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SECTION XXXVII

THE ANALYTICAL CHEMISTRY OF NITROGEN AND ITS COMPOUNDS

BY K. I. VASU

Nitrogen occurs in widely different forms in nature. Its compounds, organic as well as inorganic, exhibit a broad variety of complex chemical and physical properties. As a consequence the analysis of nitrogen and its compounds involves almost all the available techniques and the recipes for their application vary in detail from sample to sample. In this account the methods are reviewed and an attempt is made to show how any technique must be modified in a wide variety of applications.

Elemental nitrogen is rarely present in natural or synthetic products: even when 'dissolved' in metals it may exist as a nitride, and atmospheric nitrogen finds its way into oxysalts, oxides and proteins. Nitrogen compounds are used as fertilizers, explosives, synthetic fibres, plastics, paper, and find application in an oil refinery and in metallurgy. Nitrogen is thus present in a variety of materials, both organic and inorganic, natural and synthetic, but in all its compounds it forms only covalent linkages with other atoms. The field of nitrogen analysis is consequently wide and varied.

Moreover the very extensive literature includes many examples of the application of a particular analytical method to samples of different origins and subject to different degrees of contamination, as will indeed be evident in the following surveys.

METHODS OF DETECTION AND IDENTIFICATION OF NITROGEN AND ITS COMPOUNDS

Physical Tests

A spectrograph is usually used to detect nitrogen. However the lines depend on the presence of other gases: with oxygen, they are at 3995, 5008 to 5005, 3437 to 3329, 5680 to 5667, and 5045A. in decreasing order of sensitivity; in the presence of hydrogen, the lines are 5008 to 5005, 5680, 4643, 4607 and 5942A.[1] The cyanogen lines, formed in the presence of carbon, are well known. Nitrogen in solids and in solutions can be detected spectroscopically if the sample is sparked at reduced pressure. An activated form of nitrogen which appears to be atomic nitrogen is produced by a high-voltage discharge at low pressure; the examination of its emission spectrum leads to its identification.[2] A newer technique of detecting nitrogen is by observing the collision excitation of nitrogen molecular band heads by optical means under conditions where the gases are bombarded, under moderate pressures, with high-energy radioactive particles; the limit of detection of nitrogen in helium is about 1 part in 10^{10} by this technique.[3]

Chemical Methods

ELEMENTARY NITROGEN

Nitrogen reacts with magnesium or calcium at red heat forming the nitride which is readily decomposed by water, acids or alkalis giving ammonia, identified by standard reagents. The formation of the nitride with magnesium, Maquenne's calcium–magnesium mixture, or titanium serves as sensitive tests for nitrogen.[4,5]

AMMONIA AND AMMONIUM SALTS

White pumice impregnated with iodic anhydride or iodic acid and fuming sulphuric acid turns green-brown on contact with ammonia or other oxidizable gases.[6,7] Alkalis liberate ammonia from ammonium salts or its derivatives; the ammonia from this or other sources is detected by a wide choice of methods: its smell; its reactions with moist litmus; the formation of prismatic, yellow crystals of hexamethylenetetramine picrate formed in presence of formaldehyde and picric acid[8]; the characteristic crystals formed with picric acid in ethyl malonate or alcohol–glycerol mixtures[9,10]; the colour produced by phenol and hypochlorite[11]; the pink or red coloration on zinc nitroprusside exposed to sulphur dioxide[12]; the yellow-black colour with copper sulphate and hydrogen peroxide[13]; Nessler reagent[14–17]; formaldehyde, hæmatoxylin or *p*-nitrodiazobenzene[17,18]; the precipitation of a silver mirror from silver nitrate and tannin or formalin[19,20]; the colour reactions with diazotized amines[21]; the change in dielectric constant of a mixture of zinc oxide and a catalyst[22]; the change in electrical conductivity on passing the gas through an ionizable liquid[23]; the curious furrows produced on a drop of oleic acid[24]; the reaction with thymol and hypobromite producing a dye which is soluble in ether and xylene[25,26]; the change of suitable reagents on silica or titania gel[27]; the molybdenum indigo ($Mo_2O_5 + MoO_3 + H_2O$) formed from MoO_3 in the presence of atomic hydrogen from decomposed ammonia[28]; characteristic crystals formed with picrolinic, picric or styphnic acid[29,30]; the formation of purple needles of ammonium permanganate[31]; the colour change of copper salts saturated with ammonium salts or picric acid, or of silica gel impregnated with iron, copper, cobalt or nickel salts[32–34]; the luminescence, under ultra-violet light, of zinc sulphate and oxine[35]; and the formation of a black precipitate on a micro-slide when a solution is treated with a crystal of iodine,[36] or by formation of manganese dioxide from manganous and silver nitrates.[37]

OXY-COMPOUNDS

Nitrites and nitrogen peroxide can be detected by the manganese–oxalate test; a solution of manganous salt and potassium oxalate in acetic acid turns red in the presence of nitrites or nitrogen dioxide, the colour deepening on the addition of hydrogen peroxide or lead peroxide.[38,39] Antipyrin in presence of mercuric sulphate and potassium ferricyanide, lead peroxide or potassium persulphate develops a red coloration with nitrites.[40,41] Ludwig has described an apparatus for detecting evolved gases from nitrous acid or nitric acid after reduction with zinc.[42] Nitrites produce a deep red colour with *p*-aminophenol in acetic acid.[43] In presence of thiosulphates, acidification of nitrites gives a yellow, green or brown colour depending on the concentration[44,45]; an orange colour is developed on the addition of ferrous sulphate.[45] It has been pointed out that the resorcinol test for nitrites is attended by several difficulties.[46–49] A yellow to red colour is produced by nitrites in presence of aniline, 1:2:4-tolylenediamine, or *m*-toluidine,[45,50,51] or a blue cloud with diphenylamine.[52–56] Diethyldiphenylurea gives a red colour with traces of nitrates and nitrites in sulphuric acid solution.[57] Diazotization of primary amines and coupling with other organic substances has been the basis of several tests for nitrous acid and nitrites. Some other colour tests for nitrous acid, nitrites and nitrous fumes (NO_2, N_2O_3 etc.) are based on reactions with the following: neutral-red in presence of acids[58–60]; the Griess reaction with sulphanilic acid and α-naphthylamine, benzidine, β-naphthol or other phenols and amines[12,61–70]; hydrostrychnine[71,72]; phenolsulphonates[73]; methyl orange[74]; *m*-phenylenediamine, antipyrin, or starch–iodide (zinc, potassium) mixture[17,75]; naphthionates[76]; apomorphine[77]; diphenylamines or other complex amines, aminophenols pyramidones or phenols, sometimes in the presence of hydrogen peroxide or copper salts[78–88]; indigosols[89]; chrysean[90];

Magdala red[91–93]; phenol, resorcinol, orcinol, and thymol, all being variations of Rodillon's test[94–96]; azorubine[97]; Trypan red[98]; azo-xylidic reagent[99]; silver nitrate[100–102]; a capillary method with hydroquinone[103]; *o*-aminobenzaldehyde-phenylhydrazone[104]; copper salts[105]; toluylene red (neutral red)[106]; and safranine.[107] Generally, diphenylamine, brucine and indigotin are sensitive to nitrites. Iodide tests are too sensitive to other oxidizing agents. The Bismarck Grey test demands extremely precise control, and errors due to isomerization impair the test with α-naphthylamine. But the colour of azo-compounds from xylidine and β-naphthol is stable and sensitive.[108]

Nitrates are easily detected by reduction to nitrites which are easily detected by any of the methods enumerated above; nitrites, if initially present, are decomposed by boiling with urea, sodium azide or sulphamic acid.[109,110] The usual brown ring test with ferrous sulphate and sulphuric acid can be made more sensitive if a little hydrochloric acid is added; the diphenylamine reaction is not as specific and sensitive as the brown ring test.[111–116] Ultra-violet spectroscopy has been found practicable for the detection of nitrites and nitrates.[117] A purple or red colour is formed with *N*-(α-naphthyl)ethylenediamine in presence of nitrate and nitrite.[118,119] A micro-crystalloscopic test with mercury organic compounds has been described for nitrates and nitrites.[120,121] The depolarizing action of nitric acid on a platinum electrode can be utilized to detect its presence.[122] Formation of nitrobenzene with benzene and sulphuric acid can be identified by its odour; the nitrobenzene can in turn be reduced to aniline which with mercuric chloride forms fuchsin having the reddish violet colour; the violet colour with sulphuric acid and nitrobenzene in presence of nitric acid is also a specific test for the last.[123–126] Dianiline selenate gives a blue colour with nitric acid.[127] A red colour is observed with 2:4-diamino-6-hydroxypyrimidone and sulphuric acid; the test can be performed like the brown-ring test.[128] Similar colour reactions are: with 1:5-dihydroxyanthraquinone[129]; with diaminophenol[130]; with β-methylumbelliferone[131]; with arylimino-8-dinaphthoxazines[132]; with brucine–glycerol mixture[133]; and with pentachlorophenol.[134]

NITROGEN IN ORGANIC COMPOUNDS

Nitrogen in organic compounds is usually detected by Lassaigne's test or Castellana's method: the organic compound is fused with sodium or potassium, sometimes with iron powder, so as to fix sulphur and avoid formation of thiocyanates, or with a mixture of alkali metal carbonate and magnesium, or sodium peroxide. The resulting cyanide is detected by conversion to ferrocyanide or by other methods; heating the organic substance with sodium carbonate and sucrose or with zinc dust or dextrose also forms cyanides.[135–146] Decomposition of nitrogenated substances with lime or soda lime and finely divided copper or zinc causes evolution of ammonia which is identified by the silver mirror with silver nitrate and methanol or by Riegler's *p*-nitraniline–sodium nitrite reagent.[147–153] Oxides of nitrogen produced by heating organic substances with lead peroxide and manganese dioxide can be detected by sulphanilic acid–α-naphthol reagent; with manganese dioxide inorganic ammonium salts, hydrazine, albuminous and alkaloid substances, and, in fact, all classes of organic substances can be tested for nitrogen.[154,155] A wet oxidation with sulphuric–perchloric acid or hydrogen peroxide in presence of ferrous sulphate and acetic or sulphuric acid gives ammonium compounds which can be detected in the usual way.[156,157] Hydrogenation by the ter Meulen method (see p. 604) also produces ammonia.[158] Ammonium salts are formed on boiling the organic compound with concentrated sulphuric acid, sometimes preceded by reduction with hydriodic acid or followed by oxidation with potassium permanganate; ammonia is also formed on the hydrogenation of nitriles.[159,160] Silver permanganate has been described as a catalyst in the elemental analysis.[161] Nitrogen in all classes of materials can be oxidized by manganese oxides to yield nitric acid and detected by one of its usual methods.[162] A micro capillary method has also been described for the determination of nitrogen in organic compounds.[163,164]

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NITROGEN IN SPECIFIC CARBON-CONTAINING COMPOUNDS

Detailed schemes are available for the detection of ammonium salts, nitrates, cyanides, urea, cyanamide and related compounds.[165,166] Detection of cyanide in the presence of a variety of other anions has been effected by the typical precipitation with silver nitrate, sodium picrate, guaiacol–copper sulphate, hydroceruligone, or the Prussian Blue test[50]; complex cyanides are detected by ferric chloride, molybdic acid or ferrous sulphate[17]; thiocyanate is detected by the usual blood-red coloration with ferric salts, or by the catalytic decolorization of iodine solution in presence of sodium azide according to the reaction[18]:

$$2NaN_3 + I_2 \xrightarrow{CNS^-} 2NaI + 3N_2\uparrow$$

Permanganate oxidizes thiocyanate to cyanide which is detected by silver nitrate–methylene blue solution.[167] The bromoacetanilide test has been used to detect acetanilide in acetophenetidine.[168] Uric acid and purines are detected by the murexide test.[169] There are some colour reactions for certain chlorinated tertiary aliphatic amines with vapour detectors containing a bismuth salt and potassium iodide or nickel dimethylglyoxime, and with liquid detectors containing cobalt, bismuth and titanium salts and sodium thiocyanate.[170] Nitrous oxide is decomposed on heated platinum and the resulting oxygen can be detected with pyrogallol.[171] Specific, sensitive tests for nitrates, simple and complex cyanides and several other anions have been described.[17,172,173] Identification of alkaloids has been accomplished by the characteristic precipitates with potassium perrhenate.[167] Hyponitrous acid, present as an intermediate compound in the biological or photochemical oxidation of ammonia to nitrous acid, can be detected by the orange-red colour with resorcinol and potassium periodate; hydrazine, if present, can be detected with Fehling's solution when 'red copper' is precipitated.[174] 3:5-Dinitro-*p*-toluic acid forms toluates of characteristic melting point with amines and anilines, allied heterocyclic compounds and their derivatives; the melting points of many of them are available.[175,176] Compounds containing the amidine group, such as urea, guanidine and their derivatives, can be detected by treatment with hypochlorite and α-naphthol or thymol when yellow-to-red quinonoid pigments are formed.[177]

Many other particular references are found in the literature to the detection of nitrogen compounds. For example: ammonium ion[178,179]; nitrogen pentoxide, particularly in drugs[179]; cyanide, ferricyanide, ferrocyanide, nitrate, nitrite and thiocyanate[180]; ammonia, hydrogen cyanide and nitrogen dioxide in respiratory poisons[181]; ammonia in milk by sodium potassium tartrate and Nessler reagent after precipitation of proteins by uranyl acetate[182]; ammonia in phenol–formaldehyde resins[183]; Griess reagent for nitrous acid and Nessler reagent for ammonia in drinking water[184]; cyanides, and organic nitrogen converted to cyanides on sodium fusion, by converting them to thiocyanates[185]; spot tests for cyanides, thiocyanates, complex cyanides, nitrites and nitrates[186]; toxic gases containing ammonia, nitrous gases, aniline and hydrogen cyanide[187,188]; nitrous gases in industrial atmospheres[189]; nitrites[190]; ammonia and triethanolamine in sulphonated oil[191]; ammonia and uric acid in urinary calculi and gallstones[192]; nitrite, ammonium salts, nitro-compounds, nitric esters and the combustion products of explosives and ammunition by Feigl's spot tests[193]; ammonia in war gases by means of a catalytically operated apparatus[194]; simple and complex cyanides, thiocyanate, nitrites and nitrates by means of suitable fluorescence indicators[195]; various catalytic spot-reactions, including the detection of nitrous acid formed during the reduction of nitrates in acid solution by means of zinc[196]; the colour and solubility of the precipitates of a large number of benzidine derivatives with thiocyanates, azides, complex cyanides or nitrosocyanides, nitrous acid and nitric acid[197]; microreactions of ammonia and hydrogen cyanide with the use of an electric furnace[198]; hydrogen cyanide and nitric oxide in manufactured gases[199]; urine contamination on fabrics[200]; 3-nitroso-1:3-indandione as a reagent for a variety of organic bases[201]; chromatographic separation of nitrites, nitrates and other nitrogen-containing ions[202–204]; identification of nitric and nitrous esters[205];

volatile poisons[206]; components of biological fluids[207]; a large number of gases containing combined nitrogen[208]; various resins[209]; and the difference between pyridine-type and other nitrogen compounds by means of mass spectrometry.[210]

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METHODS FOR THE DETERMINATION OF NITROGEN

Gasometric and Absorption Methods

When in admixture with other gases, elemental nitrogen is generally determined by a difference in volume after the absorption of the other gases by suitable means. The method, of course, fails in the presence of inert gases. When a more direct absorption method is employed, heated magnesium, lithium, magnesium-lime mixture, calcium carbide, spongy titanium and zirconium are useful absorbents for nitrogen. Adsorption–desorption processes on carbon at liquid air temperatures can also be adapted for the analysis of nitrogen in presence of hydrogen and helium.

An old, reliable, method for determining nitric oxide, *e.g.*, a measurement required in evaluating the decomposition of liquid or solid samples of nitrates, is based on the use of a nitrometer. Nitrates are decomposed by sulphamates in acid solution and the evolved nitrogen can be determined from the equation:

$$NO_2^- + HSO_3{\cdot}NH_2 \rightarrow HSO_4^- + N_2 + H_2O$$

Ammonium salts evolve nitrogen on treatment with hypobromite solution:

$$2NH_3 + 3OBr^- \rightarrow 3Br^- + 3H_2O + N_2$$

Azides evolve nitrogen on hydrolysis. The common Dumas method of oxidizing ammonium or nitrogenous organic compounds to nitrogen is still an ideal method in many cases.

In metals nitrogen can exist in both elemental form and as the nitride. Vacuum fusion methods are used to determine the total nitrogen. Soluble nitrogen is determined by treating the nitride with mineral acid and estimating the liberated ammonia; the ester-halogen reagents are used to differentiate between soluble nitrogen compounds.

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An arc passed through a gas at low pressure between magnesium electrodes forms magnesium nitride which can then be decomposed and the resulting ammonia determined. A spark discharge will convert all nitrogen to its oxides if sufficient oxygen is present: the oxides are absorbed in alkaline hydrogen peroxide and the resulting nitrate estimated.[1] Both methods are useful for residual nitrogen in noble gases.[2,3] Absorption of nitrogen by magnesium or lithium is indeed a common practice.[4–9] A method of condensation gas analysis using the principle of fractional distillation, extended by use of adsorption on silica gel or active carbon at low temperatures, has been used to determine nitrogen in presence of hydrogen, oxygen, hydrocarbons and/or helium.[10–12]

An absorptiometer for the volumetric and gravimetric analysis of gases containing ammonia, nitric oxide, cyanogen and hydrogen cyanide has been described by Moser.[13] Gas analysis apparatus (nitrometers or azotometers) has been described in the literature along with methods of operation. Absorption solutions, and their recipes, are an important part of gas analysis.[14–26] For example, mine gases or other gas mixtures are analysed for ammonia by absorption in acids, nitric oxide by solid potassium hydroxide, nitrogen dioxide by hydrogen peroxide, cyanides by alkaline ferrous sulphate and thiocyanates by dilute ferric chloride.[27–29] Nitrogen in natural gas or commercial hydrogen is determined by the difference in volume after burning the hydrogen with oxygen on a heated platinum wire or cupric oxide.[30–33] In technical gas analysis, the gas is passed with oxygen through a heated quartz capillary containing palladium and, after absorbing the resulting carbon dioxide and excess oxygen in alkaline pyrogallol, the residual nitrogen is measured separately.[34,35] Passage of the gas through heated cupric oxide will also oxidize carbonaceous gases to carbon dioxide.[36–40] The general method is thus one of combustion.[41] Instead of alkaline pyrogallol, sodium hyposulphite or heated copper can also be used to absorb oxygen.[42,43] Nitrogen is practically insoluble in alkaline pyrogallol.[44] In some cases, carbon monoxide can be absorbed by cuprous chloride and hydrogen by colloidal palladium.[45] A method of accurate determination of ammonia in natural gases is to absorb it in a suitable reagent, measure the volume of residual gas and to titrate the absorbing solution.[46] In certain gaseous mixtures, ammonia is absorbed by a moistened bead of phosphorus pentoxide.[47] Dissolved nitrogen in water is expelled when treated with a suitable solid electrolyte such as potassium hydroxide; removal of oxygen by alkaline pyrogallol leaves the nitrogen to be volumetrically determined alone.[48] In another method, the sample of water is sprayed into an evacuated bulb, the gases are dried and the oxygen removed by phosphorus when the residual nitrogen can be estimated; if necessary, nitrogen can be removed by lithium.[49]

Nitrites evolve nitrogen with sulphamic acid and nitrates are reduced to nitric oxide by the addition of acid ferrous chloride; these gases can be measured in a gas burette.[50] Oxides of nitrogen are reduced when passed over finely divided nickel at 800°C.; the resulting nitrogen can be determined volumetrically, and compared with the value for the gross amount of oxygen determined by the contraction in volume on the reduction of the nickel oxide with a known volume of hydrogen.[51] Digestion of diazo-compounds with sulphuric acid in an atmosphere of carbon dioxide evolves all the nitrogen of the diazo group as gas which can be determined in an azotometer.[52] Azotometry has been developed further for the determination of several metals through their oxines,[53,54] and of nitrous acid, aromatic amines (simple and complex), carbonyl compounds (through their phenylhydrazones), and derivatives of phenol, antipyrine and *iso*nicotinic acid.[55–60]

The Dumas combustion of nitrogenous organic compounds with copper oxide at 900°C. gives a mixture of carbon dioxide (which can be absorbed by alkali), water vapour (condensed by solid carbon dioxide in acetone), and nitrogen, the volume of which is noted in an azotometer[61–63]; the water vapour can also be absorbed by calcium chloride and the halogens by metallic silver.[64] The Lunge nitrometer is quite commonly employed in this context.[65,66] A gasometric determination of total nitrogen in serum, blood and urine involves a Kjeldahl digestion followed by

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treatment of the neutralized digest with sodium hypobromite and measurement of the evolved nitrogen.[67,68] Several other manometric methods have also been described.[69,70] The foam method, which measures the gas foam evolved during the reaction, is a modification of this process; saponin or albumin is used as foam stabilizer.[71,72] The Dumas and Kjeldahl methods are described in detail in the subsequent sub-sections.

There are several other general procedures reported in the literature for the analysis of gaseous mixtures[73–138] and are also reviewed by Templeton and Watters.[139] The analysis of the oxides of nitrogen and of the air is described in later sub-sections.

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The Dumas Method

Dumas' gasometric method for ascertaining the nitrogen content of compounds depends on its quantitative conversion to nitrogen gas and the measurement of its volume under standard conditions. The substance is burnt in a combustion tube in an atmosphere of pure, air-free carbon dioxide; an oxidizing filling, generally cupric oxide, in the tube is used as a source of oxygen. The carbon, the sulphur and the hydrogen present are converted to the respective oxides, and the nitrogen and the halogens are evolved in the free state. The halogens are absorbed by metallic silver. Any oxide of nitrogen, particularly the neutral nitrous oxide, is reconverted to nitrogen by a heated copper spiral. The resulting nitrogen is swept out of the heated tube by a stream of pure carbon dioxide and collected in a graduated vessel (the nitrometer) over concentrated potassium hydroxide solution which absorbs the carrier gas. From the measured volume of gas, reduced to N. T. P., the amount of nitrogen in the substance may be calculated. Pregl has modified the method to the micro scale.

The success of the method depends on the quantitative liberation of the nitrogen content of the substance as molecular nitrogen. This may fail in the case of polynitro-compounds unless certain modifications of the experimental conditions are made. A few compounds such as pyrimidines, purines, and porphyrins or other pyrrole derivatives form a nitrogenous charcoal when heated with copper oxide, and consequently yield low values for nitrogen. This difficulty can be overcome by using an additional oxidizing agent such as potassium chlorate or dichromate, lead chromate, copper acetate or mercuric acetate. Of these, lead chromate may slowly attack the combustion tubes. The method has been adapted to solids, liquids and gases, and is

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applicable even in the presence of elements like selenium.[1–4] Discussions of the errors involved, of the general applicability and of other aspects of the Dumas method are recorded.[5–61]

It is suggested that, after the volume of nitrogen is read in the azotometer, it is necessary to subtract 1·2% as a correction for the adhesion of potash to the glass.[62] The vapour pressure of the potassium hydroxide solution is also to be taken into account.[63] If water is used to collect the gas, it should be saturated with nitrogen at the start.[64] Several gasometers and weight azotometers have been described in the literature.[65–68]

MODIFICATIONS FOR SPECIAL CLASSES OF COMPOUNDS

Some diazoketones are catalytically decomposed with loss of nitrogen while they are mixed with cupric oxide or copper; in such cases, accurate results are obtained if the substance, prior to the start of the combustion, is kept away from contact with cupric oxide.[69] In analysing refractory substances like pyrimidines and purines, some potassium chlorate is placed in a porcelain boat in the unoccupied portion of the combustion tube, in front of the copper oxide filling; in this way, the nitrogenous residue is subjected to an atmosphere of oxygen from the potassium chlorate.[70] Occasionally, some neutral gases are formed and mistaken for nitrogen; the danger of misinterpreting such results is to be avoided.[71] Difficultly combustible substances may form paracyanogen which decomposes to cyanogen at 860°C. and results in the formation of cuprous cyanide; the latter decomposes only at bright red heat and hence retains some nitrogen.[72]

Some experiments indicated that the sample vapour is likely to enter the azotometer without combustion when the fixed furnace temperature is only 600°C.; this does not occur above 750°C. As a precaution to avoid this, cobalt oxide is added directly to the sample because this was found to have a higher oxygen-generating capacity; nickel oxide was also found suitable for the complete combustion.[73,74] The possibility of incomplete combustion is also overcome by recycling a mixture of the combustion products through the combustion tube until a constant residual volume is obtained; any organic residue is completely oxidized by passing oxygen over the hot residue.[75] If the combustion of organic nitro-compounds is carried out in oxygen alone from the start, all the nitrogen is obtained as its oxide, and precautions should be taken for this.[76] Burning over copper oxide in a moist carbon dioxide–oxygen mixture with excess of oxygen, and removal of excess oxygen by heated copper, has been successful with compounds hard to burn completely.[77–79] For such refractory substances as pyrimidines, purines and pteridines, a modification of the Dumas–Zimmermann method[35] with cobalt sesquioxide as an oxidation catalyst and copper acetate for temporary filling of the combustion tube has been found successful.[80] Samples of such substances can also be burnt in pure oxygen and the combustion products passed over copper oxide and platinum at 725°C.; the oxygen is then removed by hot copper, and the nitrogen swept into potash solution by a stream of carbon dioxide.[81] Or it can be burnt with copper oxide in a platinum boat in a stream of carbon dioxide or oxygen.[82,83] Generally it is found that adsorbed air on copper oxide does not introduce any appreciable error in the analysis.[84]

TECHNICAL DETAILS—TUBE PACKING

The combustion tube is connected at one end to the nitrometer and at the other end to the source of carbon dioxide. Essentially the sequence of packing is (*a*) coarse wire-form copper oxide, approx. 10 cm., and (*b*) reduced copper spiral, wire, and gauze, sometimes preceded by some silver wire, approx. 5 to 6 cm. The copper has to be replaced when its bright coppery appearance disappears, but normally suffices for about 50 analyses. This is then followed by temporary fillings, fresh for each experiment: (*a*) sufficient wire-form copper oxide followed by another layer of powder-form copper oxide, 4 to 12 cm., (*d*) sample suspended in more fine copper oxide or buried in a large excess of copper oxide, with or without potassium chlorate, lead chromate or copper acetate, and (*e*) another oxidized copper spiral or copper oxide wire, approx. 5 cm. Each successive layer of filling should be held in place by a pad of ignited asbestos, approx. 2 to 3 cm. in thickness. The dead space is filled with glass rods. Modifications of this packing process are sometimes necessary, for example, (i) to prevent incomplete decomposition of nitrogen oxides[85–87]; (ii) to eliminate errors in difficultly combustible ring compounds such as pterins[88]; (iii) to avoid too rapid combustion and yet to allow it to be complete[89]; (iv) to decrease the reduction of carbon dioxide[90–92]; (v) to perform a rapid combustion process[93]; (vi) to attain complete combustion of compounds which form tars, graphitic carbon or methane upon pyrolysis[94]; and (vii) to avoid loss of volatile compounds.[95] To avoid too rapid a combustion of the sample, the boat is filled with powdered copper oxide and an equal weight of calcium carbonate.[96] If the substance is explosive, it is mixed with some benzophenone or glucose.[97,98]

INTERFERENCES AND ERRORS

The gases that interfere in the Dumas method are oxygen, carbon monoxide and oxides of nitrogen. Reduced copper removes oxygen and reduces oxides of nitrogen to nitrogen, but this requires a temperature of 500–600°C. at which carbon dioxide dissociates over copper. Raney nickel is a better reagent for the removal of oxygen and for the complete reduction of oxides of nitrogen without causing dissociation of carbon dioxide.[99] For the analysis of refractory compounds and long-chain fatty acid amides, a permanent tube filling of nickel–nickel oxide mixture followed by hopcalite was found suitable; hopcalite helps in the recombination of dissociated carbon dioxide. Another auxiliary furnace at 700°C. containing highly active precipitated cupric oxide plus 1% of magnetic oxide of iron facilitates the complete oxidation of methane if present.[100–105] In another modification, the sample is burnt with a mixture of copper and nickel oxides with a final layer of copper over it. A great variety of nitrogenous products can be satisfactorily analysed in this way, including silver nitrate which gives low values by the conventional Dumas procedure.[106] A method has been described for the regeneration of the copper oxide filling in the combustion tube.[107]

Production of air-free carbon dioxide and its supply at a constant flow rate has been described by several authors.[108–117] Pure carbon dioxide can be generated from sodium bicarbonate or a fused mixture of sodium and potassium carbonates and sulphuric acid.[118–120] Some authors recommend the generation of the carbon dioxide by heating potassium bicarbonate with zinc or from magnesium carbonate or magnesite heated in a tube outside the combustion furnace,[121,122] or contained in the closed end of the combustion tube.[123] If marble is used, it should be free from traces of pyrites which will liberate hydrogen sulphide and poison the catalyst.[72] Air present in the pores of the marble is removed by suction from the sample covered with water or calcium chloride solution.[124] Another generator is a vacuum flask nearly filled with finely crushed solid carbon dioxide connected to the combustion apparatus.[125,126] Copper containing appreciable amounts of iron or zinc should not be used; at red heat such alloys reduce carbon dioxide to carbon monoxide, but alloys of tin showed no ill effect.[127] Sodium present in the organic sulphur compounds has been found to form a coating of sodium sulphate, which permanently deactivates the combustion tube filling.[128,129] Presence of tin or boron in the compounds requires some modifications in the standard procedure.[130,131]

THE DUMAS APPARATUS AND ITS USAGE

Descriptions of the combustion furnace—micro, semimicro and macro—as well as allied processes are found in several papers.[132–136] The combustion tube is made of silica or special glass.[137] The use of special steel or copper tube with air-cooled ends has been found satisfactory for combustion.[138,139] Copper boats containing the sample and the oxidizing agent have sometimes been used.[140] Instead of attempting to expel all air by passing carbon dioxide through the apparatus, it is best to evacuate the combustion tube at the start.[121] If the stream of carbon dioxide is properly regulated better results are obtained.[141] In weighing out the sample for the Pregl–Dumas micro procedure, an ordinary balance can be used provided a comparatively large sample of the substance is ground up with a very large excess of finely precipitated cupric oxide, and an aliquot portion of the mixture is weighed.[142] Another dilution method is to employ a 1% solution of the material in carbon tetrachloride.[143] The sample is usually taken in boats of platinum, copper or nickel. In analysing tar or oils of low nitrogen content, suitable changes in the size and design of the apparatus are necessary.[144]

Addition of a small quantity of freshly precipitated mercurous oxide to the mercury serves to prevent gas bubbles adhering to the interface between mercury and potash in the azotometer.[145] The sticking bubbles can also be released by magnetically moving a piece of iron wire placed on the surface of the mercury.[146] The trouble caused by the penetration of nitrogen from the air through the rubber tubings is overcome by using the minimum length of thick-walled rubber tubing and high-quality stoppers, or by employing an all-glass apparatus.[147–151] By an analysis of the various equilibria involved in the combustion, it has been found that a working temperature of 700 to 800°C. is satisfactory for the combustion.[152,153] Variations in the sampling technique, gasometers, combustion furnaces, tubes, connections, valves and type of reagents used have been mentioned by several authors, with several improvements and modifications of the apparatus and the technique.[154–160]

Easily volatile liquids should be sealed in a capillary and placed in a projecting part of the combustion tube; during the experiment, the end of the capillary is heated electrically so that it softens and the vapours escape to the reaction zone.[161] A special procedure is necessary for introducing an air-free sample into a bulb and breaking it with a magnetic arrangement.[162] Mechanical methods or some other techniques are also described for breaking the capillaries containing the samples.[163,164] Drying and weighing of hygroscopic substances has been discussed.[165] Aqueous solutions are pipetted into the boat and evaporated under vacuum at 90 to 110°C. before the combustion procedure.[104] Several authors have described the construction of microbalances and elaborated the specific directions for the Dumas analysis.[166,167] Statistical analysis of the data from a large number of investigations indicates that the following five variables affect the precision or the accuracy of the Dumas results: (*a*) the rate of sample burner movement; (*b*) the long-furnace temperature; (*c*) the location of stop-cock or needle valve; (*d*) the average sample weight, and (*e*) the rate of sweeping with carbon dioxide.[168,169]

Some of the modifications give better results of a wider applicability. By heating the sample with copper oxide and a limited supply of oxygen sent to and fro in the combustion tube until the combustion is complete, equivalent amounts of carbon dioxide and nitrogen are formed; the total volume and that of nitrogen after the removal of carbon dioxide by potassium hydroxide enable the simultaneous estimations of carbon and nitrogen in the sample to be made.[170] For simultaneous determination of nitrogen, carbon and hydrogen, the substance is burnt with copper oxide and the products, namely, nitrogen, carbon dioxide and water vapour, are subjected successively to temperatures of liquid air, solid carbon dioxide–acetone, and room temperature, and their pressures are measured; this partial condensation method gives accurate results, even compared with other procedures.[171,172] It is also possible to absorb the nitrogen of the Dumas experiment by passing the gas over hot magnesium and recovering the nitrogen from the resulting nitride.[173] Simultaneous determination of nitrogen and hydrogen can be accomplished if the conditions are regulated: the oxygen for combustion is obtained from copper oxide; and silver foil and reduced copper are used for the reduction of the nitrogen oxides.[174] It is stated that nitrogen can be determined accurately without mixing the sample with copper oxide if a temperature of 1000°C. is used for the combustion.[175]

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The Kjeldahl Method

Many nitrogen compounds, inorganic or organic, when treated with pure, concentrated sulphuric acid at a high temperature in the presence of suitable catalysts, are decomposed with the formation of ammonia which is fixed by the acid as ammonium sulphate. The mixture is made strongly alkaline and the ammonia distilled into an excess of standard acid; back titration with standard alkali gives the amount of ammonia and hence the nitrogen content of the sample. The method thus involves three steps: digestion, distillation and titration.

THE DIGESTION PROCESS

The sample is heated with concentrated sulphuric acid in a long-necked Kjeldahl flask. In the Gunning modification, potassium or sodium sulphate is added to raise the boiling point of the acid and effect a more rapid reaction. A catalyst is required to accelerate the digestion. The common catalysts are copper oxide, copper sulphate, mercury, mercuric oxide or sulphate, selenium or copper selenate. Organic compounds are charred initially, but at the high temperature the carbon is slowly oxidized by sulphuric acid, which is itself reduced to sulphur dioxide. It is probably this sulphur dioxide that converts all nitrogen compounds to ammonia. The evolution of sulphur dioxide and trioxide is copious. Digestion has to be continued for several minutes even after the mixture is completely colourless and clear since the decomposition is not necessarily complete at this stage.

The Kjeldahl method is of especial value for the analysis of biological materials such as blood and protein and for manures and vegetable products, and, indeed, can be used with confidence upon nitrogenous compounds of most types, excepting azo-compounds and esters of nitric or nitrous acids. These require an additional reduction process, though sometimes it is sufficient to add glucose to the digestion mixture. In any case, if there are doubts of incomplete decomposition, the mixture, after cooling, is treated with a few drops of perhydrol or potassium permanganate and again boiled for a few minutes. Pyridine ring compounds require a considerable digestion time. Considerable frothing and foaming may occur during the initial stages of digestion. Addition of a small piece of paraffin may be helpful in such cases. Use of 'oleum' in the place of ordinary sulphuric acid may also prevent foaming. When hydrolysis is carried out in open flasks, the proportion of sulphuric acid and potassium sulphate or sodium sulphate must be carefully regulated in order not to cause volatilization of ammonia from the ammonium bisulphate. Use of a reflux condenser is advantageous in such cases. Addition of a little graphite is advisable to prevent overheating and glass beads can be used to prevent 'bumping'. Sulphuric acid free from ammonium sulphate and oxides of nitrogen is a prerequisite for the process. The freedom of the acid and other reagents from these substances is always ascertained by a blank experiment *e.g.*, with sucrose as the reference compound in the digestion step.

A low temperature requires too long a digestion time, while a high temperature results in loss of nitrogen. The proper temperature is obtained in the Gunning modification by adjusting the amount of sodium sulphate or potassium sulphate.[1–4] In no case should the temperature exceed 420°C.[5]

CATALYSTS

Some analysts prefer to use copper sulphate as a catalyst, with the alternatives phosphoric acid, trichloroacetic acid, potassium sulphate or selenium. Anhydrous copper sulphate apparently is the best of these. It does not dissolve completely in sulphuric acid, and the small crystals act as boiling stones to prevent 'bumping'.[6–13] An effective digestive mixture for protein and non-protein nitrogen contains sulphuric, phosphoric and perchloric acids. The digest can be treated directly for the Nessler determination of ammonia in such cases.[14]

Mercury and mercuric oxide or sulphate have been used as effective catalysts.[15,16] If a few milligrams of mercurous iodide are added instead of these, the carbonaceous material is oxidized much more rapidly.[17,18] The use of chloroplatinic acid has also been mentioned. Even a small spiral of platinum will catalyse the reaction.[19,20] In the digestion of flour, the time required to obtain a clear solution when a mixture of vanadium pentoxide and cupric oxide is used is considerably less than when either of these catalysts is used alone.[21] Selenium or selenium oxychloride has been said to be better than any of the catalysts given above.[22–31] In the initial stages of digestion, a fast reaction occurs, probably catalysed by colloidal selenium which then coagulates to droplets and the reaction rate becomes limited by diffusion and is of the first order.[32,33] Amorphous selenium is more rapid as a catalyst than copper sulphate and more economical than selenium oxychloride.[34] Selenium has the added advantage over mercuric or copper salts that it does not require a precipitant during the distillation; but it appears that there is a greater danger of losing some nitrogen during extremely long digestion times with selenium than with other catalysts.[35,36] This is probably due to the combustion of the ammonium salt to nitrogen. However, if the digestion is properly carried out there is no loss of nitrogen.[37–39] The use of selenium with mercuric oxide is probably more satisfactory than the use of either substance separately.[40,41] On boiling selenium or tellurium with sulphuric acid, selenous and tellurous acids are formed which are supposed to be the active catalysts in the process; it is therefore more rational to use selenous acid rather than selenium itself for the digestion.[42,43] In the absence of mercury, catalysis is accomplished by the reversible redox reaction:

$$Se + 3H_2O \rightleftharpoons H_2SeO_3 + 4H^+ + 4e$$

and in the presence of mercuric oxide, by the reaction

$$Se \rightarrow H_2SeO_3 \overset{H_2O}{\rightleftharpoons} H_2SeO_4 + 2H^+ + 2e$$

However, the use of a selenate is not practical.[44,45] Selenium or selenium oxide with one or more of sodium sulphate, potassium sulphate, mercuric oxide or sulphate and copper oxide or sulphate is used in many cases; with these mixtures digestion is stated to be complete in a shorter time, particularly when phosphorus pentoxide is also present. Such recipes have been successfully employed in the analysis of rubber, coke, coal, cereals, alkaloids and refractory heterocyclic compounds.[46–67] Copper selenite or mercuric selenite used as a single catalyst, or the use of copper and selenium with a sulphuric–phosphoric acid mixture, reduces considerably the time for complete digestion.[68–72] Tellurium is also a good catalyst, either alone or with copper sulphate or ferrous sulphate.[73,74] In the study of the mechanism of the Kjeldahl process, palladium, platinum, mercuric sulphate, silver sulphate, vanadium pentoxide, selenium dioxide, tellurium dioxide and copper sulphate are positive oxidation catalysts, but their relative activities vary with the temperature and the substance oxidized.[75] The presence of the third and fourth group elements of the periodic system retards the Kjeldahl digestion considerably unless an accelerator like selenium or platinum is present simultaneously.[76] Although copper is the cheapest catalyst, selenium remains the most energetic and can be regenerated. It is also found that the maximum effect of catalysts soluble in sulphuric acid is proportional to their maximum solubility under the given conditions.[77] A mixture of equal parts of ferrous sulphate and selenium has proved slightly more efficient than copper–selenium mixture.[78] Some other catalysts mentioned in the literature are: manganese dioxide[79,80]; mercury with persulphate and perhydrol[81] or with potassium phosphate and ferric sulphate.[82] For the analysis of collagen in leather, the catalytic efficiency was found to be in the decreasing order: mercury, selenium, copper, manganese. A mixture of sodium sulphate, copper sulphate and sodium selenate gives complete digestion in a short time, and with this catalyst the Kjeldahl method is found to be superior to hydrogenation methods.[83]

TREATMENT OF SPECIAL CLASSES OF COMPOUNDS

Even with the use of catalysts low values are often obtained for nitrogen, probably owing to incomplete decomposition of the compound. In some of such cases, addition of potassium permanganate at the end of the digestion has been suggested.[84–90] A similar, chromic acid, modification gives low values even though it has been suggested for soil analysis.[91,92] Perchloric acid can be employed with or without selenium, but sometimes this may cause loss of nitrogen, particularly in presence of sodium sulphate.[93–100] Hydrogen peroxide and persulphates are effective oxidizing agents, but are to be added before the sulphuric acid; for plant and biological materials, the peroxide is to be added after a preliminary ashing with sulphuric acid.[101–114] Proteins and their derivatives should be oxidized with bromine and hydrogen peroxide.[115] Selenium–permanganate or mercuric oxide–potassium sulphate mixtures are also said to give good results for proteins and amino acids.[116–119]

More troublesome substances like sodium nitrate, nitriles, oximes, osazones, semicarbazides, hydrazines and hydrazones, azobenzene and polynitro-compounds require a preliminary digestion with benzoic acid and sulphuric acid followed by a reduction digestion with zinc dust and alcohol in acid solutions before final treatment with phosphoric–sulphuric acid mixture and potassium sulphate with or without additional catalysts. Low values in some of these cases are due to the evolution of some nitrogen.[120,121] Substances like cyanamides and nitrates require a reducing agent during the Kjeldahl determination. Copper powder is found sufficient in certain cases while the nitrates require a mixture of iron wire and copper oxide.[122] Certain substances in coal, particularly the pyridine derivatives, are converted to ammonium sulphate only slowly and hence a longer digestion is required.[123]

The direct digestion, even if improved by the use of catalysts, is unsuitable for a number of substances, especially the azo compounds and those where the oxygen is attached to nitrogen as in the esters of nitrous and nitric acids.[124] In these compounds there is a tendency to lose some of the nitrogen as gaseous nitrogen or as an oxide unless an additional reduction step is included prior to the digestion process. There are several prereduction processes suggested: (*a*) For many non-volatile organic compounds, such as the azo-dyes or nitro-amines the complete reduction can be effected by the mere addition of glucose, thiosalicylic acid or even cotton cellulose to the digestion mixture and then carrying out the initial heating very gently. Sodium hyposulphite is another suitable reducing agent with copper sulphate as a catalyst. Instantaneous reduction of azo compounds occurs also with powdered, reduced copper or an excess of cuprous oxide added to the concentrated sulphuric acid.[125–132] (*b*) Volatile compounds and substituted hydrazines and semicarbazides should be preheated in a bomb-tube with some hydriodic acid for 1 hr. at 200° to 300°C. before they are transferred to the digestion flask.[133–135] In certain cases, they can be reduced directly in the Kjeldahl flask by means of hydriodic acid to which have been added a few particles of red phosphorus. After boiling for half an hour, the hydriodic acid is boiled off before the mixture is digested with concentrated sulphuric acid and the catalyst mixture.[136,137] This procedure gives satisfactory values for ring nitrogen of some heterocyclic compounds. It has, however, been found that the nitrogen-bearing ring is attacked only under certain structural conditions.[138] (*c*) Diazo compounds may be analyzed by heating with phenol for a short time before being digested. The phenol couples with the diazo compounds to a stable azo-derivative. The phenol–sulphuric acid mixture should be poured on quickly when ammonium salts, nitrates and nitro-compounds are present.[139,140] (*d*) For total nitrogen in the presence of nitrates or nitrites in plant material, the sample extract is first reduced with titanous chloride after adding sufficient alkali. For nitrites reduction by titanous chloride in acid solutions containing zinc powder and platinum chloride catalyst should be conducted before the normal digestion.[141,142] (*e*) Determination of nitrogen in aromatic nitro-compounds includes reduction by zinc or iron prior to the Kjeldahl digestion. Pure iron reacts too quickly but a mixture of iron filings and copper oxide serves to accomplish the accurate determination of phenylhydrazone, antipyrine, brucine and dinitrobenzene. For similar compounds a cadmium–potassium sulphate mixture seems to give good results except upon phenylhydrazine for which selenium–potassium sulphate mixture proved to be a suitable catalyst. Reduction with hyposulphite has also been successful. Occasionally addition of pyrogallic acid is sufficient. The use of α-naphthol–pyrogallol mixture gives results better than those achieved with salicylic acid or thiosalicylic acid.[143–154] (*f*) To include nitrate nitrogen in the analysis of soils, fertilizers and plant materials, the substance is first treated, overnight, with sulphuric acid containing salicylic acid and then heated with sodium

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thiosulphate to reduce the nitro-group before digestion.[155] Instead of salicylic acid, phenol can be used. Good results are obtained by first reducing with Devarda's alloy in alkaline solution.[156] Metallic cadmium in the presence of orcinol reduces nitrates to ammonia.[157] Lower results are obtained if chlorides are present; in such cases, the Devarda's reduction is better.[158] Digestion of steels can be accomplished with a sulphuric–hydrofluoric acid mixture in the presence of hydrogen peroxide.[159] For zirconium, a hydrochloric–hydrofluoric acid mixture is better.[160] Simple Kjeldahl digestion gives only the total nitrogen, and an ester-halogen method has to be used to differentiate between the individual nitrides and dissolved nitrogen in an alloy.[161] Nitrogen in organo-arsenic compounds can be determined by normal Kjeldahl digestion; the arsenic remains in the solution when ammonia is distilled off. If any chlorine is present, digestion is carried out in a current of air which carries away the chlorine.[162] Presence of halogen compounds during the digestion introduces appreciable errors, the extent depending on the nature of the halogen compound.[163]

TECHNIQUE

During the digestion, copious evolution of sulphur oxides occurs: methods of removal have been described.[164–172] One particular method employs a closely fitting acid-resistant gas-pervious ceramic septum or an alundum thimble, called the Hengar tube, within the neck of the Kjeldahl flask. After use the Hengar tubes are prepared for re-use by heating to redness.[173] Bumping during digestion is avoided by the addition of alundum or carborundum chips.[174] If foaming occurs, particularly with foods and feeding stuffs, polyethylene and vinylidene chloride are found to be good antifoams during digestion.[175]

SUMMARY OF DIGESTION PROCEDURES

An analysis of the various methods of digestion shows that they fall into four groups which use: (*a*) only catalysts, (*b*) only oxidizing agents, (*c*) an elevated boiling point achieved with potassium sulphate or sodium sulphate, (*d*) any combination of the preceding groups, some of them in a constant flow of air. Milbauer has discussed the relative merits of these methods or the combinations thereof. The catalysts employed in the study include selenium, mercury, copper, manganese, vanadium and molybdenum.[176] Kirk has reviewed the present status and future developments of semimicro, micro and ultramicro Kjeldahl processes. The following digestion factors are considered: amount of sulphuric acid used, amount and kind of added salt, catalysts, oxidizing agents, reducing agents, and time and conditions of digestion.[177]

RECOVERY OF AMMONIA BY DISTILLATION

In several cases the ammonia in the digest can be determined directly without distillation by methods such as: (*a*) alkali hypobromite and iodimetry[178–180]; (*b*) gasometry[181]; (*c*) colorimetrically with ninhydrin or after addition of Nessler's reagent[182, 183]; and (*d*) formol titration.[184–186] However, better results are obtained if the ammonia is distilled from the digest and determined separately in the distillate. For this, the cooled digest is basified and the flask is promptly connected to a condenser with its delivery tip dipping *under* the surface of a measured volume of standard acid. Boiling chips or other expedients are employed to avoid 'bumping' of the liquid, and a trap between the flask and condenser is used to prevent alkaline spray from being carried into the receiver. To ensure complete recovery of ammonia, the mixture in the flask is distilled until about one-third or more of the liquid has passed over. Aeration or steam distillation can also be applied to assist the recovery of ammonia. Descriptions of several types of distillation and absorption sets and methods are found in the literature.[187–219] The most important is the Parnas–Wagner apparatus.[220] The residue after digestion is cooled and treated with a concentrated solution of sodium, potassium or barium hydroxide or alkali metal carbonate or magnesium oxide.[221] The heavy metals such as copper and mercury used as catalysts have to be precipitated with potassium sulphide, sodium sulphide, sodium disulphide or sodium hypophosphite before the ammonia is distilled off; the substitution of sodium thiosulphate for potassium sulphide or sodium sulphide is permissible.[222–224] A few milligrams of zinc dust is found beneficial if added along with sulphides because this will reduce any mercuric ions to metallic mercury, but the hydrogen evolved may, by splashing, carry alkali over to the distillate.[225–227] Some Kjeldahl digests of biological specimens are likely to contain amines and similar volatile compounds which also distil; the presence of alkaline earth metals markedly influences the amount of these in the distillate and renders the titration inaccurate unless bromothymol blue or phenol red is used as indicator.[228–230] Instead of the simple, direct distillation, it is possible to distil ammonia in a current of steam from a separate generator. The use of steam obviates bumping and shortens the time of distillation. Addition of zinc aids the release of traces of ammonia retained in the digest.[231–244] Vacuum distillation is also feasible and gives maximum recovery of ammonia.[245–250] Studies on the effect of aeration on recovery of ammonia illustrate that it has distinct advantages with respect to time and lack of bumping.[251–255] If foaming occurs during the distillation, a few drops of alcoholic cholesterol, stearic acid, or mineral oil are found to be good preventives.[256–258]

TITRATION OF THE DISTILLATE

Direct condensation of the ammonia distillate and a simple titration against standard acid using dimethyl yellow–methylene blue indicator is straightforward; the use of boric acid or a measured volume of standard acid to catch the distillate is stated to be unnecessary.[259, 260] A method has been described for the direct titration of the Kjeldahl ammonia in which a solution of nickel ammonium sulphate is used as the absorbent; the ammonia absorbed is titrated with acid using methyl red as indicator.[261] In some cases the ammonia is absorbed in sodium dihydrogen phosphate and titrated electrometrically or with bromocresol green indicator. Absorption in phosphoric acid and titration with hydrochloric acid using mixed bromocresol green–methyl red indicator has also been suggested.[159, 262, 263] In general practice, standard sulphuric or hydrochloric acid is used in the receiving flask for ammonia, and the excess is titrated with standard alkali. Bromocresol blue, benzoyl auramine G and methyl red with or without methylene blue are used as indicators.[264, 265] Titration in the cold introduces an error due to the carbonate in the alkaline solution and titrating hot gives an incorrect end-point because of the hydrolysis of ammonium sulphate; hence an initial titration to an apparent end-point in the cold is followed by heating to boiling to expel the carbon dioxide, cooling quickly and titrating to a fresh end-point.[266] A conductimetric titration has been found to give satisfactory results.[267] The Winkler modification with boric acid is as accurate as this but far easier to perform. Only one standard solution of acid is required. The ammonia is absorbed in a solution of boric acid, usually about 4 to 5%, the concentration of which is of no concern so long as the amount of acid is more than equivalent to the ammonia to be absorbed. The reaction is:

$$NH_3(g) + HBO_2 \rightarrow NH_4^+ + BO_2^-$$

Boric acid is such a weak acid (K_a about 10^{-10}) that its anion, BO_2^-, is a strong base and its titration with a strong acid is feasible:

$$BO_2^- + H^+ \rightarrow HBO_2$$

The standard acid required in the titration is directly equivalent to the ammonia absorbed, and to the nitrogen content of the sample. Satisfactory indicators are: bromophenol blue or bromocresol green either alone or with methyl red or coccine, methylene blue with methyl red, blue blossoms of butterfly pea, and *p*-nitrophenol.[9, 268–284] An ingenious method of avoiding the titration step is to measure the pH or conductivity of the boric acid–ammonia solution and read the ammonia content from calibration curves.[285, 286] If the distillate for the titrimetric analysis is boiled so as to sharpen the end-point, some ammonia is likely to be lost.[287] It is stated that acid potassium iodate, $KH(IO_3)_2$, can be used as a titrating acid.[288] An iodimetric titration with phosphorus pentoxide as catalyst has been suggested. Ammonia in microquantities in the distillate is usually estimated colorimetrically by the Nessler reagent.[19,290,291]

MODIFIED PROCEDURES

There are several variations of the Kjeldahl process. The residue after a wet combustion with chromic acid or perchloric acid gives ammonia when made alkaline; this ammonia can be distilled off and estimated in the usual way.[292–294] Many substances can be easily digested by heating with sulphuric acid and potassium iodate.[295,296] During Kjeldahl digestion in a stream of oxygen, the nitrogen is converted to ammonium sulphate while the carbon is converted to carbon dioxide which can be absorbed and estimated separately.[297] For amides, treatment with alkali followed by distillation in a current of air is all that is required for the recovery of the equivalent ammonia.[298] Nitrogen in the range of 1 to 100 p.p.m. can be determined by quantitative reduction to ammonia by high-pressure hydrogenation with a nickel catalyst; the ammonia formed is absorbed on acidic alumina and is determined by a conventional Kjeldahl distillation.[299] On heating the organic material with magnesium powder out of contact with air, all nitrogen is converted to magnesium nitride; this can then be treated by the Kjeldahl method and the nitrogen estimated.[300]

APPLICATIONS AND COMPARISONS

Materials which have been successfully analysed for their nitrogen content by the Kjeldahl method are: calcium cyanamide; nitrates and nitrogen fertilizers; insoluble metallic nitrides of titanium, vanadium, niobium, tantalum, iron and aluminium; prussian blue pigments; cereals, flour, food-stuffs, condiments, milk and milk-products, cheese, meat, eggs, honey, coffee, wine; albumins and amino-acid; blood; wine; leather and hides; tobacco; wool; textiles; cyanoethylated cotton; mustard; horn; rubber; glue; gelatin; beet products; oil cakes; enzyme preparations; hydrazine derivatives; nitrobenzenes, azo- and azoxybenzenes; alkaloids containing pyridine, piperidine or other groups; soil; sewage sludges; water; coke, coal and shale oil. In fact, there is some way to convert the nitrogen of any organic substance into ammonium sulphate, although it may well be that one and the same catalyst is not always suitable.

Comparison of the Kjeldahl and Dumas methods shows that the former always gives a lower result, the difference in some cases being negligible and in others considerable. The Kjeldahl method has been variously named after Gunning, Arnold, Wilfarth, Dyer, Winkler, Wagner, Parnas, Friedrich and Pregl, for their respective contributions to the development, modifications or improvements of the technique.[301] The method is explained in terms of an initial oxidation followed by hydrolysis.[302] The general Kjeldahl procedure with the various aspects of modifications and improvements in the apparatus as well as the technique will be found in detail in many papers,[303–502] of which the more recent[503–505] are of particular value.

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Determination of Nitrogen in Metals

VACUUM FUSION AND HOT EXTRACTION METHODS

Vacuum fusion and hot extraction methods involving vacuum degassing below the fusion point are employed for the determination of total nitrogen (and other gases), both elemental and combined, present in metals and alloys. The fusion method consists of melting the metal in a graphite crucible, preferably within a graphite spiral resistor or a high-frequency induction type vacuum furnace. Sometimes tin, molten iron or platinum is used as flux for the sample. Oxygen and oxides react with the crucible to produce carbon monoxide. Nitrides and hydrides as well as free nitrogen and hydrogen form the gaseous elements. Thus oxygen, hydrogen, carbon monoxide and nitrogen are the common ingredients of the gases evolved. Analysis for the individual components involves extensive manipulations: (*a*) Nitrogen can be absorbed in metallic calcium vapour and the resulting calcium nitride analysed chemically after decomposition to ammonia[1]: (*b*) The gases are removed by a diffusion pump to reservoirs, subsequently circulated over hot cupric oxide, and after removing the carbon dioxide and the water vapour (formed from oxygen and hydrogen), the unoxidized and unabsorbed nitrogen is determined.[2] In the analysis of steels, the presence of manganese and aluminium above a certain limit affects the results.[2,3] (*c*) For measuring the gases, an Orsat apparatus with an explosion pipette and platinum capillary can be used; however, nitrogen may undergo slight conversion to oxides in the explosion pipette.[4,5] (*d*) Nitrides of the various constituents of steel can be fractionally separated since their decomposition temperatures differ.[6] (*e*) Some of the components of the evolved gases could be condensed to solid and the residual gas determined; for example, carbon dioxide is frozen out with liquid nitrogen.[7–10] (*f*) At times, the analysis is completed by a mass spectrometric determination of the composition of the evolved gases.[11–14]

There are several improvements upon the vacuum fusion method or hot extraction method in recent years.[15–37] Aluminium and manganese are volatile at the vacuum fusion temperature, and the deposits of these elements on the cooler parts absorb and retain considerable quantities of the evolved gases[38,39]; metal film deposition within the apparatus is absent if excessive heating is avoided or if small amounts of steel devoid of nitrogen are added to the sample.[40] Sometimes addition of tin or tin–iron alloys prevents 'gettering' by manganese, magnesium and titanium.[41,42] For lanthanum, a nickel bath is used. The vacuum fusion method can be adapted easily to the microscale.[43,44] For total nitrogen, a vacuum fusion in presence of sodium peroxide, occasionally moderated by the addition of alkali metal carbonates or a mixture of lead oxide and lead chromate, is found useful and gives more accurate results.[45–49]

WET METHODS

The nitride nitrogen in metals can be determined by a wet method so that dissolved nitrogen is obtained by difference. The sample is dissolved in ammonia-free acid when the nitride decomposes to form the ammonium salt. Many special steels contain ingredients which cause the formation of nitrides insoluble in mineral acid. In such cases digestion with perchloric acid with some phosphoric or sulphuric acid and hydrogen peroxide, selenium, potassium sulphate and copper sulphate is essential.

Titanium can be dissolved in hydrofluoric acid.[50–59] The solution is then made alkaline and sometimes treated with zinc or graphite; the ammonia is finally distilled off and estimated in a suitable way. Generally the estimation is carried out by titration against an acid using one of the following indicators: iodo-eosin, methyl orange, methyl red–methylene blue, alizarinsulphonate, bromocresol blue or bromocresol green.[60–69] Occasionally distillation can be avoided altogether.[70–72] An iodate–iodide method has been found very satisfactory.[73,74] Colorimetric determination employs Nessler reagent,[75–81] phenol–chloramine or phenol–hypochlorite reagent,[82,83] or other reagents.[84,85] Combined nitrogen in aluminium can be estimated in a similar manner.[86,87] But such specimens can be directly dissolved in sodium hydroxide in a suitable apparatus so that the ammonia can be distilled off directly for estimation.[88–90] Incombustible inorganic substances such as thorium nitride can be fused with sodium pyrosulphate in a platinum boat and the nitrogen collected over alkaline pyrogallol solution.[91] The nitrides thus fall into three groups: (*a*) nitrides such as those of iron, manganese and silicon which are soluble in dilute acids, (*b*) metalloid nitrides soluble in sodium hydroxide after separation of the acid-soluble group, and (*c*) nitrides, mostly of titanium and vanadium, which are insoluble in either dilute acid or alkali and for which special methods have to be applied.[92,93] Values close to the Kjeldahl procedure are obtained by a hydrogenation method: nitrided iron is heated to 450° to 500°C. with hydrogen and the ammonia produced is estimated.[94] There are reports of a bromination method also.[95]

The ester–halogen reagents are commonly employed to differentiate between soluble nitrogen compounds. For example, if a sample of steel is extracted with bromine and methyl acetate under reflux, all the iron is dissolved and the residue contains aluminium nitride; this can be estimated by a standard procedure.[96–100]

MISCELLANEOUS PHYSICAL METHODS

There are several physical methods of analysis. The concentration of nitrogen in iron and steel threads is found to effect proportional variation in the logarithmic decrement of the torsional oscillations when it is made part of a torsion pendulum.[101] When the damping of the elastic vibrations of a metal wire around its axis is plotted against temperature, a maximum is observed, the height of which depends on the amount of nitrogen dissolved in the iron.[102] The residual resistance of a perfect crystal lattice varies almost linearly with impurities and this finds use in estimating the amount of nitrogen.[103] An internal friction method has been used for determining nitrogen in α-iron.[104] There are reports of the applicability of the electron probe *X*-ray microanalyser for the determination of nitrogen in metals. Electron, proton or ion bombardment methods have been reported.[105–107] The indicator method with radioactive elements is used to follow an element in a chemical reaction, and stable isotopes of nitrogen have been used to determine nitrogen in steels.[108] By ionic bombardment of iron containing nitrogen in solid solution and chemical combination, part of the nitrogen is liberated at normal temperature, part by displacement with hydrogen, and the rest by vacuum fusion at 900°C. The distinction between nitrogen in solid solution and that present in combined form can be made by this method.[109]

COMMENT ON APPLICATIONS

Methods of nitrogen determination in iron, steel, aluminium and other metals and alloys are very important in industry in a variety of circumstances. Most of them are based on the methods listed above. It must, however, be conceded that judicious variations and modifications of the procedure are necessary for specific cases. Every step is important—sampling, reagents used, temperature employed, recovery of ammonia or nitrogen, and their estimation.[110–163]

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Spectrometric Methods for the Determination of Nitrogen

In recent years many of the classical wet chemical methods have been replaced by physical methods which are quicker and often easier. Of the physical methods, spectrometric methods are the most popular. These include mass spectrography and isotope analysis, and optical spectroscopy such as emission spectrography, interferometry, flame photometry, microwave spectroscopy, infra-red and ultra-violet absorption spectroscopy, colorimetry and spectrophotometry. Nitrogen and a variety of its compounds—gaseous, liquid or solid—can be analysed by any one of these methods.

MASS SPECTROMETRY AND ISOTOPE ANALYSIS

A mass spectrograph is a device for ionizing and accelerating the ions and measuring the mass-to-charge ratio of the ionized atoms or molecules. Since the charge of the ions generated in the instrument is often known and is frequently ±1, an analysis of the mass of the ions formed is possible. Identification and quantitative analysis are easily carried out. The presence of ammonia in the gases evolved from dry batteries has been analysed in a mass spectrometer.[1] Other analyses include those of mixtures of nitrogen with one or more of gases such as carbon monoxide, carbon dioxide, hydrocarbons, oxygen, hydrogen, oxides of nitrogen, noble gases and a variety of others.[2–14] Semiquantitative analysis of nitrogen in organic compounds can be accomplished by pyrolysing the material with oxygen and hydrogen and analysing the product gases with the mass spectrometer.[15] Combustion with cupric oxide or nickel oxide followed by the reduction of the oxides with copper gives nitrogen; this 'Dumas' nitrogen along with neon as internal standard is introduced into the spectrometer for quantitative analysis. The precision is $\pm 1 - 2\%$ of the nitrogen present.[16–18] A simple diffusion method has been described for the mass spectrometric analysis of ammonia in many samples of nitrogeneous metabolic products and chromatographic fractions.[19] Analysis of ^{15}N is of great significance in several studies. Isolation of the mixed molecule ^{14}N^{15}N and its spectrometric estimation gives results close to those obtained by a gas density balance.[20] Oxygen-free nitrogen prepared from air can be used as a standard in the analyses of nitrogen samples enriched with ^{15}N. There are several other studies with nitrogen isotopes.[21–27] In the analysis of nitrogen in organic compounds, a Kjeldahl digestion to form ammonia and the decomposition of ammonia to nitrogen by means of alkaline hypobromite is necessary. By-products such as nitrous oxide and carbon dioxide can be frozen out with liquid air to avoid their interference.[27,28]

The use of isotopes of different masses or activity is of immense importance in analytical chemistry. Nitrogen has isotopes ^{14}N and ^{15}N. The heavy isotope is added in known amounts to a known weight of the sample, the mixture equilibrated and the isotopic ratio determined by a mass spectrometer.[29] The method has been applied to the study of protein metabolism and the analysis of nitrogen in organic compounds.[30–34] In order to produce accurate spectrographic analysis of nitrogen and its isotopes, the element is incorporated in a chemical compound which is capable of enhancing the separation of the corresponding spectral lines characteristic of its isotopes.[35]

Traces of nitrogen can be determined by using the technique of activation, addition of carbon carrier, and combustion and assay of carbon dioxide by gas counter tube.[36] A new method is based on the difference in the infra-red absorption spectra of isotopic molecules.[37] From the activity of oxygen formed by the $^{14}\mathrm{N}(d, n)^{15}\mathrm{O}$ nuclear reaction, it is possible to determine traces of nitrogen.[38]

EMISSION SPECTROSCOPY

Flame photometry and spectrographic methods depend on measuring the intensity of the light emitted by the material which is excited in a flame, an arc or a spark. The lines or bands can be resolved and their intensities determined with a densitometer. The appearance of cyanogen bands is a very delicate test for the compounds of nitrogen admitted to a hydrocarbon flame in the form of a gas such as nitrous oxide, ammonia, nitroethane, piperidine, cyanogen, hydrogen cyanide, methylamine and some other nitrogenous organic substances.[39] The intensity of the cyanogen band at 3883A. is proportional to the concentration of organic nitrogen present in a solution atomized into the inner cone of a gas flame.[40] A possible method of analysis of a mixture of hydrogen and nitrogen is by measuring the brightness of spark spectra with an optical wedge.[41] Nitrogen diluted with hydrogen or carbon dioxide is spectrographically determined by the lines 5008 or 3437A., respectively.[42] By use of condensed sparks, a quantitative spectral analysis of mixtures of nitrogen with hydrogen, oxygen, helium or argon can be made down to a limit of 0·05 to 0·03%.[43,44] Strong lines characteristic of nitrogen appear in the visible and ultra-violet regions when materials are excited in an intermittent arc with very high current density and reduced pressure.[45,46] Mixtures of nitrogen with carbon dioxide and oxygen are sealed in a glass tube and the spectra produced by external electrodes connected to the poles of a high frequency generator; intensity ratios are measured for a nitrogen band at 3159·3A. and a carbon monoxide band at 3134·4A. The coefficient of variation is ±3·5%.[47] Bands at other wave-lengths can also be selected.[48–52] A similar method is used for the microdetermination of ^{15}N. Accuracy with the high frequency torch discharge method is found to be higher than that of the usual low-pressure discharge method.[53,54] Substitution of helium, argon or other gases for air near the carbon electrodes enables the arc-spectrochemical analysis to be extended to include nitrogen.[55,56] A low-voltage spark pulse discharge or intermittent arc between samples kept in an atmosphere of carbon dioxide and analysis of the resulting spectra can be used for the determination of nitrogen in steel. However, such methods fail for nitrogen in titanium.[57–59]

A gas interferometer divides a beam of light through the gas into a number of beams and reunites them to produce interference, the nature of which depends on the components of the gas.[60] Interferometers have been developed with different arrangements and used either alone in spectrographs or as an addition providing higher resolution. The method has been applied to the analysis of a benzene–ammonia–hydrogen sulphide mixture,[61] argon–nitrogen–hydrogen mixture,[62] mine gases,[63] nitrogen–argon mixtures[64] and gases from mineral water.[65] An ingenious method of gas analysis depends on the change of gas pressure in an interferometer chamber with compensation of the current difference instead of compensation with a revolving glass plate.[66]

ABSORPTION SPECTROSCOPY

The nitrogen content of noble gases has been determined by a method based on the enlarged absorption of a mercury band.[67] Monochromatic *X*-rays of wave-lengths lying on either side of the *K*-absorption edge of nitrogen are used for its determination in tissues; one may determine 10^{-10} to 10^{-12} g. of nitrogen.[68] Nitrogen in hydrogen and in nitrogenized alloys can be determined spectroscopically by the intensity measurements at the absorption lines 3995A.[69] Nitrogen mixed with carbon monoxide, carbon dioxide, hydrogen or air can be analysed by an infra-red gas analyser consisting of a light source and a sample cell with rock salt crystal windows and two divisions, one filled with the sample gas and the other kept *in vacuo*.[70]

By far the easiest way of determining a species, such as a nitrogen compound, in solution is the colorimetric and the allied spectrophotometric method. The absorption of radiation by an atom, ion or molecule is related to a change in the electronic distribution in their orbitals. Electronic transitions close to a nucleus involve a high energy change and occur only in the *X*-ray or the far ultra-violet region. Shifts in the outer levels are associated with the u.v. and visible ranges. Vibrational and rotational changes within a molecule are also accompanied by electronic transitions, but the absorption spectrum consists of several lines, sometimes merging into bands for a complicated molecule. Simple inorganic ions have bands in the u.v. regions, but addition of a suitable reagent will produce a coloured complex, the characteristics of which can be studied in the visible range. Vibrational spectra involve low energy transitions and the associated absorption is in the near infra-red, while the absorption corresponding to rotational level changes are in the far infra-red and microwave regions.

Hauss has reviewed the application of the photoelectric colorimetric method for the estimation of various nitrogen compounds and has listed the reagents used.[71] A precise colorimeter has been constructed to determine nitrite, nitrate, amino-nitrogen and ammonia in water. Ammonia is determined with the phenol–hypochlorite solutions or Nessler reagent.[72–76] For the analysis of bread, beef, fish, milk, cheese, tobacco or leather, the material is first digested with sulphuric acid and hydrogen peroxide until colourless, sometimes with a suitable catalyst; it is then neutralized and treated with Nessler's reagent, and the colours compared with a standard.[77] Distribution of nitrogen in a grain of barley is obtained by the analysis of successive microtome sections of the grain.[78] Total nitrogen in presence of carbon, phosphorus or silicon can together be determined colorimetrically.[79–81] Analysis of blood, urine and tissue fluids for their ammonia, uric acid, creatinine and allantoin content can be carried out with the same solution. Certain factors, however, influence the colorimetric determination of amino-acid nitrogen. Insufficient washing during filtration is a possible error in determining small quantities of ammonia.[82–84] Nitrogen in soils and plant tissues is satisfactorily estimated by means of a spectrophotometer: ammonia by the Nessler reagent, and nitrates by phenolsulphonic acid.[85,86] Microdetermination of nitrogen in clinical conditions also employs Nessler's reagent.[87,88] In determining amino-nitrogen, β-naphthoquinonesulphonate is used as the colorimetric reagent; the excess of reagent is bleached by the addition of acid, formalin and sodium thiosulphate when a stable colour is produced.[89,90] Constructional details of photoelectric colorimeters have been given by several authors.[91,92] Colours of ammonia solutions treated with Nessler's reagent are measured at 450, 475 and 500 mμ.[93] Spectrophotometric methods are also useful in the determination of ammonia in plating baths and of the nitrogen in metals and sintered carbides; the method is as sensitive as the polarographic or titrimetric methods.[94–96] A variety of colorimetric methods can be used for the analysis of traces of nitric oxide, but none of them is specific for this. One of the oldest and widely used method is the Griess reaction of diazotization of sulphanilic acid by nitrous acid and subsequent coupling with α-naphthylamine. If nitric oxide is converted to nitrate, phenoldisulphonic acid or 3:4-xylenol can be nitrated or diphenylamine can be condensed with the nitrate to give coloured compounds which can be used for its estimation. Nitrates also react with brucine, strychnine, ferrous sulphate or pyrogallolsulphonic acid to give suitable colour reactions. A solution containing nitrous acid turns purple upon adding first α-naphthylamine and then phenoldisulphonic acid, and yellow on adding the reagents in the reverse order. Both these are used for its colorimetric estimation; major interference is from iron, aluminium, lead, copper and sulphide.[97] The colorimetric determination of ammonia, nitrites and nitrates will be comprehensively treated in their respective sub-sections.

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Miscellaneous Methods

Many of the following physical, chemical, and physico-chemical methods for the analysis of nitrogen and nitrogen compounds are unique in several respects; and some of them are fast and accurate enough to warrant industrial popularity. Of these, the ter Meulen–Heslinga method of destructive catalytic hydrogenation is applicable to a wide variety of nitrogenous organic substances. The hypobromite and formol titration procedures are apparently specific for ammonia and amino compounds. Of the other methods, some might be specific for certain nitrogen compounds, but many are applicable to the analysis of other substances in the gaseous, liquid or solid states.

THE HYDROGENATION METHOD

The ter Meulen–Heslinga[1,2] method is based on the destructive catalytic hydrogenation of nitrogenous organic substances and measuring the ammonia evolved. The substance is heated in a current of purified hydrogen and the mixture of gases formed by the volatilization or decomposition of the compound is passed over a catalyst, usually nickeled asbestos; all the nitrogen is converted to ammonia which can be absorbed in standard acid or in potassium hydrogen diiodate solution. If the compound contains sulphur, chlorine, bromine, or iodine a little soda-lime is placed in the tube beyond the nickel-asbestos. The catalyst has to be heated to 250 to 350°C. if nitrogen-evolving substances such as hydrazine compounds are to be analysed.[3] The rear part of the combustion tube should be heated much more strongly so as to 'crack' the distilling compound and render its hydrogenation complete. The method gives satisfactory results with substances which cannot be examined by the Kjedlahl process. Even compounds such as pyridines and quinolines, and natural products such as grass and hay, have been analysed satisfactorily.[4] With substances such as albumin, meat and cheese, low results are often obtained, probably owing to the loss of nitrogen in the carbonaceous residue. Presence of sulphur reduces the life of the catalyst. In these respects the method is improved by mixing the substance with finely divided nickel along with nickel formate which is easily reduced by the hydrogen.[5] For the determination of nitrogen in coal and coke, an iron combustion tube is used and the sample is mixed with equal parts of sodium carbonate and sodium hydroxide.[6,7] The use of reduced iron catalyst enables the determination of nitrogen in amino and heterocyclic compounds to be performed.[8] In determining nitrogen by the hydrogenation method in iron tubes, a synthesis of ammonia from atmospheric nitrogen takes place, which causes high values; to avoid this error, the air is forced out of the system by pure carbon dioxide.[9] A description of the apparatus, preparation of the catalyst, and the modifications and improvements of the technique can be found in a large number of references.[10–19]

HYPOHALITE AND OTHER OXIDATION METHODS

Ammonia and urea react with alkaline hypobromite liberating an equivalent amount of nitrogen:

$$2NH_3 + 3NaOBr \rightarrow 3NaBr + 3H_2O + N_2$$
$$CO(NH_2)_2 + 3NaOBr + 2NaOH \rightarrow 3NaBr + Na_2CO_3 + 3H_2O + N_2$$

Manometric measurement of the evolved nitrogen or the iodimetric estimation of the unused excess of hypobromite leads to an evaluation of the amount of urea or ammonium salt present. The chief merit of the hypobromite method is the rapidity of the analysis. The results obtained are considered to be sufficiently accurate for most medical requirements of the urea content of urine. However, urea in solution is always in equilibrium with a small amount of ammonium cyanate, and consequently the full amount of nitrogen is not evolved; in fact, all calculations are based on a value of 95·7% of the theoretical. In the case of ammonium salts 97·5% of the nitrogen is evolved. An apparatus which uses a brine solution to equalize the inside and outside pressure has been described.[20] For accurate results the alkalinity has to be properly adjusted.[21] A bromate–bromide mixture to which potassium iodide is added after the completion of the oxidation reaction is sometimes used instead of hypobromite solution.[22,23] For the reaction:

$$2NH_4^+ + 3Br_2 + 8OH^- \rightarrow 6Br^- + N_2 + 8H_2O$$

the best pH is between 7·5 and 9·5 for which a borax buffer is used.[24] For organic nitrogenous materials a Kjeldahl digestion followed by perhydrol treatment or distillation is necessary before the hypohalite oxidation procedure.[25–27] But the method has been found unsuitable for determining small quantities of ammonia in biochemical investigations.[28] The proteins can be removed by treatment with trichloroacetic acid, and the non-protein nitrogen determined iodimetrically after conversion to ammonia.[29,30] Addition of boric acid prevents interference by reducing sugars, and cadmium sulphate is used to precipitate sulphur compounds.[31,32] In carrying out the hypobromite method, the solution must be freshly prepared, the temperature should not rise above 18°C. and exposure to sunlight should be avoided. The errors arise from the instability of the reagents, from the rates at which the residual nitrogen reacts and possibly to some unknown catalyst. Instead of titrating iodine with sodium thiosulphate it may be extracted in toluene and the colour of the solution measured.[33] If the solution is properly buffered, bromine will oxidize ammonium salts completely to nitrogen and the excess bromine can be determined iodimetrically:

$$2NH_3 + 3Br_2 \rightarrow 6HBr + N_2$$

Sodium bicarbonate, borax, acetates, or a mixture of disodium and monosodium phosphates are suitable buffers. In presence of excess alkali or iron, part of the ammonia might be oxidized to nitrite or nitrogen dioxide. By the use of the phosphate buffer the proper pH is maintained and the adverse effect of iron eliminated.[34–36] The invariable presence of a little bromate as an impurity in hypobromite solutions apparently causes some error in the results; this is avoided by producing bromine *in situ* by the interaction between potassium bromide and calcium hypochlorite. The method has been used for the estimation of ammonia, hydrazine and urea solutions.[37,38] An iodimetric method is suitable for the estimation of phenylhydrazine derivatives:

$$C_6H_5{\cdot}NH{\cdot}NH_2+2I_2 \rightarrow C_6H_5I+N_2+3HI$$

The sample is poured into a known volume of iodine solution and the excess determined by titrating with sodium thiosulphate.[39] The iodimetric method is preferred to the acidimetric method for determining nitrogen of the Kjeldahl digest since the pH is ideal for the reaction with the iodate–iodide reagent.[40,41] The iodimetric method for amino-nitrogen gives systematic errors, particularly when large amounts of mineral salts are present.[42]

A method of estimation of amino-nitrogen is based on the reaction between carbon disulphide and amino acids in mildly alkaline medium to give the dithiocarbamic acid derivative the —SH group of which is oxidized by iodine with the consumption of four atoms of the halogen.[43] A novel iodimetric method for ammonia is to precipitate with Nessler reagent, reduce the precipitate with formalin and agitate with iodate–iodide solution until the mercury is dissolved; the excess iodine is back-titrated with thiosulphate.[44] A method for the rapid iodimetric determination of nitrogen in nitro, nitroso, *iso*nitroso and diazo-compounds is based on the fact that hydrogen iodide, acting as a reducing agent under high pressures and elevated temperatures, liberates an equivalent amount of iodine characteristic of every azo functional group.[45]

A chlorate oxidation method has been described for the estimation of nitrogen in plant extracts, ammonium salts, asparagine, pyridine, alkaloids, proteins, amines, amides and nitrates.[46] Wet-ashing of organic compounds by heating with concentrated phosphoric acid and potassium iodate in a current of carbon dioxide gives an equivalent amount of nitrogen which can be collected in an azotometer; the method cannot be used for volatile compounds, for ring nitrogen or for nitro and nitroso groups.[47,48]

FORMOL TITRATION

Ammonium compounds and amino-acids are easily estimated by formol titration. The reaction of formaldehyde with ammonium ions is as follows:

$$4NH_4^+ + 6HCHO \rightarrow (CH_2)_6N_4 + 4H^+ + 6H_2O$$

The acid formed is titrated with a standard base. Both the ammonium solution as well as the formalin should be neutralized before mixing.[49] The titration is carried to a pH of 9 either with a glass electrode or suitable indicators. The method can easily be adapted to estimate the ammonium salts in the Kjeldahl digests of nitrogenous materials.[50,51] Amino-acids formed from proteins and polypeptides can be determined by a formol titration, and the method is applicable to products of the cheese industry[52] and the sugar industry,[53] to hydrolyzates of meat[54] and to other materials.[55] Reaction between the formaldehyde and the amino groups of amino-acids sets free an equivalent amount of carboxylic acid which is titrated with alkali.[56]

PHYSICAL METHODS

A thermal conductivity method has been employed for the continuous analysis of nitrogen, nitrous oxide, ammonia and other gases. The method can be manual or automatic. The thermal conductivity on which the operation of the instrument depends is very nearly independent of atmospheric pressure or the rate at which the gas flows through the system. The instrument gives a continuous reading, making intermittent withdrawal and analysis of gas samples unnecessary. However, the instruments afford no qualitative analysis, and the quantitative analyses are successful only in certain special cases such as the measurement of nitrogen and hydrogen in a mixture during the synthesis of ammonia, or the determination of nitrous oxide in air.[57–66] The method is very often employed as a detector after chromatographic or diffusion separations.[67] In a modification, the effect of a non-homogeneous electric field on the convection current in a paraelectric gas around a heated platinum wire is measured. The gas mixture passes through two congruent channels along two heated platinum wires forming the branches of a Wheatstone bridge. One wire is surrounded by a non-homogeneous electric field from which the other wire is shielded. If one component of the mixture is paraelectric, the difference in resistance of the two wires is a function of its concentration. The method has been tested on mixtures of ammonia and air, and of ammonia, nitrogen and hydrogen.[68]

A variety of gases such as carbon dioxide, nitrogen dioxide, ammonia, sulphur dioxide and hydrogen in simple gas mixtures and flue gases can be analysed by recording manometrically the differential pressure between the gas and air, under constant pressure, passing (effusing) through a capillary or orifice. The relation between the density and viscosity of the gas and air has to be taken into account. In most cases the differential pressure between the gas and air is almost a linear function of the percentage of gas in the mixture.[69,70] In an apparatus which determines the difference in vapour pressure between pure argon and a mixture of argon and nitrogen, the difference gives the nitrogen content of the mixture.[71,72] Fractional separation by distillation of a mixture of carbon monoxide, nitrogen, hydrogen and hydrocarbons has been accomplished, but the method has been applied to quantitative analysis only recently.[73,74]

A discharge tube with a hollow electrode is sufficiently sensitive to detect nitrogen in argon to a few tenths of 1%. A quantitative spectral analysis is also fully possible through the photometric measurement of the lines.[75]

An acoustic gas analyser for determining the velocity of sound in a gas has been constructed; it is particularly suitable for mixtures of argon, helium, nitrogen and oxygen. With this apparatus it is possible to determine the percentages of helium and nitrogen in the whole mixture with an accuracy of approximately 1%.[76] The method is applicable to any mixture of gases. The identity of the component gases must be known or assumed and not more than two can be present when their percentages cannot be determined by other means. The degree of sensitivity will be proportionate to the difference between the densities of the component gases.[77,78] The acoustic gas analyser has been used for the analysis of mixtures of oxygen, nitrous oxide, and ether with or without nitrogen.[79] In a modified version of this principle, a speaker is attached to one end of a gas cylinder with a microphone at the other end, and the circuit is connected through an amplifier with a frequency indicator showing the characteristic frequency number of each gas to be tested. The apparatus is useful for determining the ratio of hydrogen and nitrogen to be used for ammonia synthesis.[80] A phaseometric optical-acoustical method has been developed whereby nitrogen and oxygen could be determined directly in mixtures with carbon dioxide to within $\pm 0{\cdot}5\%$.[81]

A sorption method is based on the existence of critical desorption temperatures for gases adsorbed on activated carbon. At these temperatures, the individual gases can be removed quantitatively *in vacuo* from the adsorbed surface. By use of a hot-wire manometer, a rapid analysis is possible for coke-oven gas samples containing nitrogen and nitrogen oxides, or of binary mixtures containing nitrogen and carbon monoxide, methane, oxygen or argon.[82–85]

A new differential X-ray absorption method can be employed for the analysis of oxygen–nitrogen mixtures.[86] Transmission measurements of β-particles (from ^{35}S) through gases have been used for the analysis of mixtures of nitrogen with helium or oxygen; the partial pressures of the gas mixtures vary approximately linearly with the logarithm of the transmitted number of β-particles.[87]

By use of an electron microscope, K-levels of carbon, nitrogen and oxygen were found using an exposure of less than one second; quantities down to 10^{-16} to 10^{-14} g. could be determined.[88] In another method, ionization probability curves produced by an essentially monoenergetic electron beam rise linearly from the ionization potential for an increase in electron energy of several volts. The slope of these curves is a linear function of the pressure. The ionization potentials of carbon monoxide and nitrogen differ enough for their curves to be resolved sufficiently so that the two gases can be determined in mixtures. Also, for specialized cases, an ionization chamber can be used in place of a mass spectrometer.[89]

In a magnetic method, the gas stream is divided between two capillaries in the same way as an electric current in Wheatstone bridge. A sensitive differential manometer is connected in the position corresponding to the galvanometer. Opposite arms of the 'bridge' are placed between the poles of a magnet, and the change in viscosity of the gas caused by the magnetic field is reflected by a change in pressure, which often is a linear function of composition. Mixtures of oxygen, nitrogen and carbon dioxide can be analysed by this method.[90]

Chromatographic separations have been made with nitrogen, nitrous oxide, nitric oxide, carbon monoxide, carbon dioxide and hydrocarbons by passing over charcoal or silica gel as adsorption medium and hydrogen as the eluting gas. The determination of the thermal conductivity was used in the analysis. From the migration velocity of the zones in the procedure, it is possible to calculate the adsorption energies.[91–95] The method has several other applications.[96,97] When katharometers are used with nitrogen or carbon dioxide, it is impossible to obtain any measure of chromatographic column efficiency in the region of the peak inversion temperature.[98] Calcium zeolite, Molecular Sieve Type A, gives excellent results in the analysis of small gas samples.[99]

A sensitive method for determining nitrogen in argon depends on the maintenance of an arc within the gas stream by the application of a uniform current and the continuous measurement of the arc voltage which indicates the percentage of nitrogen.[100] A similar approach would be the measurement of the voltage drop due to a low-current positive column discharge across electrodes placed in a glass tube containing the gaseous mixtures of rare gases with molecular impurities of nitrogen or carbon monoxide. In application, a fluorescent lamp can be tested in a few minutes or the method could be utilized to discover the impurities in commercial rare gases.[101]

In an infra-red gas analyser constructed with a nickel–chromium wire as light source, the sample cells having silica windows, a gas-filter and a lead sulphide photoconductive cell, mixtures of nitrogen and methane can be analysed.[102]

Nuclear reactions induced by high-energy protons and deuterons have been applied to the analysis of nitrogen on surfaces to a depth of several microns.[103]

The atom concentration of a nitrogen–noble gas glow discharge has been determined by attaching a diffusion slot leading to a space where the recombination of atoms is effected by catalysts; this results in an equivalent pressure difference.[104] In an attempt to detect atomic nitrogen in the upper atmosphere, ethylene is released from a rocket and the artificial chemiluminescence produced by the gas clouds is observed and recorded photographically. The colour and intensity of the image is related to the chemical reaction between ethylene and atomic nitrogen.[105]

CHEMICAL AND PHYSICO-CHEMICAL METHODS

In the adsorption method, non-coagulable nitrogeneous compounds, also called rest nitrogen, are estimated by adsorption on colloidal iron or fibrin powder.[106,107]

Conway's diffusion method[108–116] can be adapted to the chemical analysis of ammonia and urea. The diffusion method has been used successfully in the analysis of organic nitrogen. By means of a Kjeldahl digestion[112] the nitrogen is converted to ammonia, and in this form the nitrogen is analysed by the diffusion method: the solution is made alkaline and gaseous ammonia diffuses into a receiver containing boric acid (usually admixed with glycerol),[111,113] sodium dihydrogen phosphate,[108,112] Nessler's reagent[109,116] or sulphuric acid.[113] The method is satisfactory on a microscale.[110,112] Urea,[108,109,116] amino-acids and glutamine[116] can be determined provided they are hydrolysed to give the equivalent ammonia.[108–116]

Certain gases such as ammonia can be continuously analysed by automatically recording the changes in electric conductivity of a solution that has been exposed to the gas.[117] The determination of nitrogen in gaseous mixtures has been accomplished by oxidation with excess oxygen in an electric arc and absorption of soluble nitrogen oxides in alkali; the change in conductivity gives the percentage of nitrogen in the gas.[118]

By means of an electroscope, a radiometric method has been devised for the microanalysis of ammonia.[119] In one method, traces of ammonia are distilled into a known volume of dilute hydrochloric acid and the loss in acidity determined by its effect on radioactive lead carbonate or other lead compounds.[120, 121] Precipitation of the substance in conjunction with the radioactive thorium-*B* also serves as an indicator.[122]

The amount of ammonia produced in the hydrolysis of its salts or in the equilibrium with the ammino-complexes such as silver diammine salts can be determined in a special apparatus where the equality in the vapour pressure of a common volatile constituent distributed between two liquid phases is studied.[123] The distribution ratio of ammonia between water and chloroform has been found to be 35·82 in favour of water at 25°C.[124]

A gaseous absorption method for the analysis of nitrogen in argon or other inert gases employs magnesium or a 1 + 4 mixture of magnesium + calcium oxide for the absorption of nitrogen. The magnesium nitride formed is hydrolysed and the ammonia determined in the usual way.[125–128] The method has been modified for the analysis of nitrogen in organic substances. Combustion of a sample in the presence of powdered magnesium forms the nitride which can be analysed by standard methods.[129]

Separation of the constituents of a gas can be effected by condensation at -205°C. At this temperature there remains an incondensable fraction of nitrogen, hydrogen, carbon monoxide and methane. Carbon monoxide is removed after oxidation over iodine pentoxide, and hydrogen and methane are burned with oxygen over incandescent platinum wire. The nitrogen remains as residue.[130] In a method applicable to the determination of nitrogen in noble gases, a spark discharge converts all the nitrogen to nitric oxide which is absorbed in alkaline hydrogen peroxide and the resulting nitrate is estimated.[126]

With the acid of a thermobalance, gravimetric methods of analysis for a variety of nitrogen compounds have been devised: the ion determined, the precipitants, the weighing forms and the temperature limits for satisfactory drying are given in Table 1.[131]

Table I.—Thermogravimetric Data for Nitrogen Compounds

Ion	Precipitant	Precipitate	Temp. limits (°C.)
CN^-	$AgNO_3$	AgCN	<237
CNS^-	$AgNO_3$	AgCNS	<224
	$CuSO_4$	CuCNS	<300
	$BaCl_2$	$BaSO_4$	780–1200
	$NiSO_4$ + pyridine	$Ni(CNS)_2(C_5H_5N)_3$	110–130
CNO^-	$AgNO_3$	AgCNO	<138
	semicarbazide	$NH_2CONH \cdot NHCONH_2$	<90
$Fe(CN)_6^{4-}$	luteocobaltic chloride	$8Co_3O_49Fe_2O_3$	356–1013
	$AgNO_3$	$Ag_4Fe(CN)_6$	60–229
	benzidine, Bzd	$H_4Fe(CN)_63Bzd$	<52
	benzidine	Fe_2O_3	>944
$Fe(CN)_6^{3-}$	luteocobaltic chloride	$Co(NH_3)_6Fe(CN)_6$	<151
	benzidine	Fe_2O_3	>750
N_3^-	$AgNO_3$	AgCl	70–600
$N_2O_2^{2-}$	$AgNO_3$	AgCl	70–600
NO_2^-	$AgBrO_3$	AgBr	70–946
NO_3^-	NH_4OH	NH_4NO_3	<151
	Nitron formate	$C_{20}H_{16}N_4,HNO_3$	77–228
	cinchonine	$C_{19}H_{24}N_2O,HNO_3$	39–196
	bis-(1-methylnaphthyl)amine	$C_{22}H_{19}N,HNO_3$	60–234

CHEMICAL METHODS FOR SUNDRY COMPOUNDS

Titrimetric oxidation methods are applicable to nitrites or nitrous acid, hydrazine, hydroxylamine and ammonia. Potassium permanganate is a good oxidant.[132] Milligan has reviewed the estimation of each of these compounds in presence of others.[133] The hydrazine nitrogen of semicarbazides and semicarbazones can be estimated by titration with potassium iodate.[134]

Organic compounds. In a modification of the Kjeldahl method a wet oxidation of organic compounds can be effected by acidified potassium permangate with or without platinum catalyst or by potassium iodate and concentrated sulphuric acid at 180°C. when ammonium bisulphate is formed.[135,136]

Pyrolytic methods are applicable to organic nitrogen. Simple empty-tube or sealed-tube combustion of organic compounds in presence of oxygen compares favourably with other microtechniques. The oxides of nitrogen are decomposed over heated copper and the total nitrogen estimated in the azotometer.[137,138] If nitrogenous organic compounds are sublimed in a current of dry, carbon dioxide-free air, and passed over a layer of specially prepared manganese dioxide at 400°C., nitrogen is produced which is measured as in the Dumas method.[139,140] Fusion of the substance with a eutectic mixture of sodium and potassium hydroxides in a copper tube liberates ammonia which can be estimated by the usual methods.[141] Another pyrolytic method resembling the Dumas procedure has been developed for the reaction[142]: $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$. As is well-known, the Lassaigne fusion of an organic compound with metallic sodium in a nickel bomb produces cyanide which can be estimated by suitable methods. The method cannot, however, be used for compounds containing oxygen since, in such cases, part of the nitrogen is converted to cyanate.[143,144] Fusion of amino-compounds and plant materials with sodium hydroxide and sodium acetate converts all the amino- and amide-nitrogen to ammonia.[145]

A variety of organic materials can be hydrogenated in a rapid flow of hydrogen in the presence of iron or nickel catalysts at 300–340°C.; the evolved ammonia is determined iodimetrically by treatment with potassium acid iodate and potassium iodide in the absorption liquid and back-titrating with sodium thiosulphate.[146]

A calorimetric determination of nitrogen in foods and fodders has been described; in this method it is necessary to make a correction for the heat of formation of nitric acid.[147]

Non-aminoid nitrogen such as that in nitro, azo, diazo, and aminoazo compounds is first reduced with titanous chloride before a Kjeldahl treatment and recovery of the ammonia.[148,149]

Nitrate esters. An ester of nitric acid, such as gun-cotton, will yield the acid on treatment with concentrated sulphuric acid; the mixture can be titrated with ferrous sulphate solution. The end-point is the characteristic brown colour of nitroso-ferrous sulphate complex.[151]

Diazo compounds. A new method for determining diazo-nitrogen in stable diazo-compounds consists in treating the sample with a large excess of titanous chloride and measuring the evolved nitrogen in a gas burette.[152] Nitrogen in the diazonium borofluorides is determined by decomposition with 50 per cent sulphuric acid and measurement of the liberated nitrogen in an azotometer.[153] For certain light-sensitive diazo-compounds, hydrolysis to nitrogen is effected by dilute hydrochloric acid and exposure to direct sunlight.[154]

Pyridines. Bromocyanine and β-naphthylamine give a red colour with pyridine and its homologues such as picolines, lutidines, collidine, and piperidine. Pyridine and its homologues can be separated from nicotine and ammonia by distillation from a citrate buffer at pH 3·0.[150] Basic nitrogen of pyridines can be differentiated from that of pyrroles in shale-oil distillates by titrating electrometrically with perchloric acid in glacial acetic acid.[155] Volatile amines can be distilled, on a microscale, from a Petri dish on to a strip of filter paper containing sulphuric acid; the amount of basic substance absorbed in the sulphuric acid is then titrated.[156] Pyridinium salts react with alkaline peroxides and liberate about 75% of the nitrogen in a titratable form and render the remainder accessible to standard Kjeldahl determination.[157]

Azo dyes. For azo dyes, the following method is found suitable: by the action of the halogen, preferably bromine, the azo-dye is split into a diazo component and a bromoazo component; the diazo component is then determined by coupling it with resorcinol, α- or β-naphthol, *R*-salt, or chromotropic acid, and measuring the resulting colours.[158] An oxidation method with potassium dichromate has also been suggested for azo dyes and intermediates.[159]

Cyanides, thiocyanates. Cyanides and their derivatives form an important class of compounds. During the estimation of cyanogen compounds in ammonia liquors, it is found that digestion at 70–75°C. will convert thiocarbonate into thiocyanate without affecting the cyanide, while polysulphides at 30–35°C. will convert cyanides to thiocyanates without attacking the thiocarbonate; ferrocyanide is not affected under these conditions. The method has been standardized for ammonium thiocyanate alone or in presence of ammonium cyanide, thiocarbonate or ferrocyanide.[160–163] The Kjeldahl method is found to be suitable for the determination of nitrogen in cyanides. This method is applicable when the more rapid Volhard, Liebig and Prussian blue methods fail, for example, with the insoluble, complex or non-electrolyte cyanides.[164,165] For the determination of nitrogen in the complex cyanides of heavy metals such as potassium ferrocyanide, mercuricyanide, argentocyanide, cobaltocyanide and nickelocyanide, the sample has to be heated in a sealed tube with concentrated acids at about 270°C. for an hour before it is treated by the Kjeldahl method.[166] By making use of the anticatalysis or inhibition effect of cyanides, thiocyanates and nitriles on the arsenious–ceric system catalysed by a known amount of iodide ions, traces of these nitrogen compounds have been determined.[167] For nitriles, a pretreatment with potassium iodide and sulphuric acid is necessary before the Kjeldahl procedure.[168] Nitriles and amides can be easily hydrolysed by boiling with benzyl alcohol and potassium hydroxide; the liberated ammonia is then estimated.[169]

For organic thiocyanates, the substance is refluxed with mixed sodium and potassium polysulphides in aqueous solution; the thiocyanate is then precipitated as cuprous thiocyanate and the nitrogen in the precipitate determined by the Kjeldahl method.[170] The course of the fusion reaction between ammonium nitrate and dicyanodiamide has been followed by determining ammoniacal nitrogen, nitrate nitrogen, organic nitrogen, total nitrogen, guanidine nitrate, and biguanidine nitrate.[171]

A large number of single metals and alloys can be electroplated from cyanide baths. In one method of analysis, the plating solution is made distinctly acidic and the hydrogen cyanide is distilled into a solution of sodium hydroxide. The resulting sodium cyanide is titrated with silver nitrate.[172,173] To determine free cyanide, the Liebig method, with potassium iodide as indicator, is found preferable to the Hannay titration with mercuric chloride, although satisfactory results can be obtained electrometrically with the latter method.[174] After distilling off the hydrogen cyanide, the ammoniacal nitrogen is determined by a Kjeldahl distillation; the total non-cyanide nitrogen compounds are converted to ammonia by a digestion with sulphuric acid, and the ammonia is then distilled and estimated.[175–182]

Miscellaneous. Nitrogen in carbothialdines and alkylidenethiocarbamic acids is determined by the Kjeldahl method, but the attack is rapid and complete when the mixtures are heated in a sealed tube at 330°C. for several hours with fuming sulphuric acid.[183]

The photochemical decomposition of carbon tetrachloride solutions of nitrogen trichloride gives only uncertain results.[184–189]

General references. There are several other general papers in which some mention has been made of the analysis of nitrogen compounds in organic and inorganic substances: (*a*) ammonia, ammonium compounds and their organic as well as inorganic derivatives[190–199]; the Kjeldahl, Dumas, ter Meulen and other allied microanalytical methods for nitrogen[200–251]; nitrogen-containing functional groups

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in organic compounds[252–255]; nitrogen and nitrogen compounds in lime liquors and pulping liquors,[256, 257] in furnace slags and refractories,[258, 259] in ores,[260] in glass and organic polymers,[261–263] and in metals and alloys[264]; and finally, the inorganic nitrogen compounds such as the oxyacids and their salts, thiocyanates, ammonium salts, hydroxylamines and other amines.[265–274]

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DETERMINATION OF COMPOUNDS OF NITROGEN

Determination of Ammonia

Many types of nitrogen compounds are converted to ammonia in the course of their determination. Kjeldahl digestion, hydrolysis of metal nitrides, and reduction of oxygenated nitrogen compounds are some of the common procedures in nitrogen analysis. It then becomes evident how important it is to understand the various analytical methods for ammonia. The colorimetric method is by far the most popular micro-method but other methods such as titrimetry, gravimetry, gasometry, chromatography and polarography find application at various levels.

SAMPLING AND SELECTIVE RECOVERY

It is generally by means of a special, weighed and evacuated pipette that a sample from concentrated aqueous synthetic ammonia is taken for analysis; this avoids the possibility of any loss due to evaporation.[1,2] For the determination of albuminoid ammonia, a Kjeldahl digestion is necessary.[3] Special scrubbers and adapters made of hard glass or block tin have been described for the recovery of ammonia from Kjeldahl digests.[4,5] Instead of caustic alkali, sodium or potassium bicarbonate, or lithium or sodium carbonate can be used to liberate ammonia, and mineral acids including boric acid can be used to absorb ammonia.[6–9] Zeolite has also been used as an absorbent.[10] For the determination of ammonia in presence of hydrazine, the latter has to be destroyed with acidified copper sulphate before the ammonia is distilled off from alkaline solutions.[11] However, all the ammonia is recovered, preferably by suction, even in the presence of hydroxylamine.[12] Drawing a current of air through basified soils and fertilizers recovers all the ammonia.[13–15] In normal practice, collection of a large volume of the distillate allays the fear of incomplete distillation.[16,17] A vacuum distillation is preferable, sometimes with a slow stream of air.[18–20] Ammonia in natural waters or drinking water is distilled in presence of sodium carbonate, magnesium oxide, zinc oxide or calcium carbonate while protein ammonia is determined by distillation in presence of calcium oxide and potassium permanganate.[21–23] In gas-works practice, gas-washing bottles provided with sealed-in sintered diaphragms permit efficient absorption at much higher rates of gas flow than with the early forms of Drechsel bottles.[24] In hydrocarbon feed stocks, ammonia and aliphatic amines are condensed in a sulphuric acid–acetone mixture cooled to -80°C., and from acetylene, ammonia can be extracted with sulphuric acid.[25,26] In determining ammonia in the presence of nicotine, mercuric iodide is added to form a solid compound with nicotine so that ammonia can be freely titrated.[27] Ammophos contains water-insoluble $NH_4H_2[Fe, Al(PO_4)_2],H_2O$, and an initial extraction with 10% hydrochloric acid is necessary before distillation with alkali.[28,29] In recovering ammonia from cyanide plating solutions, simple aeration is enough, but distillation under reduced pressure is preferable; ammonia is evolved rapidly in the initial stages and represents the free ammonia plus that formed by the decomposition of both cyanide and other nitrogen compounds.[30,31] A method using sodium cobaltinitrite or mercuric oxide gives excellent recovery of ammonia from alkaline solutions containing aliphatic amines such as methylamine.[32,33] During the aeration of oysters, clams and scallops, a mixture of paraffin and octyl alcohol proved excellent for preventing foaming.[34] Meat extracts have to be deproteinized with trichloroacetic acid or sodium tungstate before the addition of alkali and aeration or distillation for the recovery of ammonia; the distillation follows a first order reaction provided aliphatic amines are absent. Biological specimens retain their urea or uric acid but yield all the ammonia during partial evacuation.[35–38] Nessler's reagent gives a yellow colour in the presence of carbohydrates, and in such instances the test for ammonia can be made only after distillation.[39] In a liniment, ammonia can be extracted with acids while the non-ammonia components are extracted with chloroform.[40] Ammoniates of platinum and cobalt have to be reduced to the metal with dilute ferrous sulphate solution and sodium hydroxide whereby ammonia is completely liberated and can be distilled.[41,42] Amide complexes of mercury have to be decomposed with sulphuric acid before distilling the ammonia; in presence of amino acids, alkaline hydrolysis gives high values.[43]

COLORIMETRIC METHODS

Phenols and hypochlorites or hypochlorous acid or hypobromites give a soluble indophenol dye with ammonia. This method has been used to determine nitrogen in steels by decomposing them in acids, treating the resulting ammonium salt with phenol and sodium hypobromite and extracting the coloured product with ethers or xylene. Sodium salicylate and sodium hypobromite give a blue colour.[44–46] In some cases, ammonia is oxidized with an excess of hypobromite, the excess treated with potassium iodide and the liberated iodine estimated photometrically.[47] In an attempt to determine ammonia in urine by means of the phenol–hypochlorite colour reaction, it was found that the colour developed with phenol is the most stable. Instead of sodium hypochlorite, chloramine-*T* can also be used: the efficiency of the reaction depends on the pH of the solution.[48–53] The phenol–hypochlorite reagent is particularly useful with plant distillates where the Nessler reaction fails owing to the presence of disturbing colour shades due to substances volatile in steam.[54] When a sample containing ammonium salts is treated first with chloramine-*T* and then with pyridine–pyrazolone reagent, a purple colour is developed which can be extracted with carbon tetrachloride and studied at 450 mμ; by this method amounts of ammonia as low as 0·025 p.p.m. can be determined.[55, 56] In the phenol–hypochlorite method, ions of iron, chromium and manganese as well as sodium nitroprusside catalyse the reaction in the direction of enhanced colour development; copper ions, on the other hand, tend to inhibit colour development.[57, 58] The blue cupric ammonium solution formed by treating ammonia in an ammonium salt solution with cupric carbonate can be employed as a colorimetric method; the absorption at 700 mμ is measured.[59] The use of two drops of 5% tannin solution and one drop of 20% silver nitrate is claimed to be more sensitive than the usual Nessler test and equally convenient.[60] A simple colorimetric method for determining ammonia in air consists in passing the gas through acidified bromophenol blue indicator and measuring the change in pH with an automatic photoelectric colorimeter.[61] When ammonia reacts with thymol and hypobromite, a coloured compound, which dissolves in *iso*propyl alcohol to give a red solution, is formed; it can be determined in a Pulfrich photometer.[62] In another method ammonia is oxidized with hypobromite, and the excess of hypobromite is determined by its power to decolorize phenosafranin.[63] There is a direct spectrophotometric method utilizing the absorption maximum at 204·3 mμ which permits determination of 7 to 1000 p.p.m. of ammonia in air.[64]

The commonest method of estimating ammonia or ammonium salts in aqueous solution is by the use of an alkaline solution of potassium mercuri-iodide, the Nessler reagent. The reagent is occasionally attributed to Winkler and Folin. It is prepared by dissolving mercuric iodide in potassium iodide solution and making the resulting solution of the complex alkaline with sodium or potassium hydroxide.[65–67] It can also be prepared by direct addition of potassium iodide to mercuric salt solutions until the precipitated iodide dissolves. Koch and McMeekin have prepared a modified reagent from iodine, potassium iodide and pure mercury.[68] The reagent kept in a white glass bottle is better than that kept in a green bottle. If supplied in ampoules, the alkali may react with the glass and further addition of alkali is necessary to restore its effectiveness before use.[69] The solution contains the ion $[HgI_3]^-$ and possibly $[HgI_4]^{2-}$. With traces of ammonia or ammonium ions in water, a yellow to brown colour or, with larger amounts, a brown precipitate, is formed. The composition of this is given as NHg_2I,H_2O, but it is also said to be $NH_2Hg_2I_3$[70]:

$$NH_3 + 2KHgI_3 + 3KOH \rightarrow NHg_2I{\cdot}H_2O + 5KI + 2H_2O$$

Interference in the test arises when some coloured and certain colourless ions are present or when certain aliphatic or aromatic amines, organic chloramines, acetone and aldehydes are present; these yield different colours or a turbidity. The effect of cations can be minimized by adding some tartrate solution. Moreover colorimetric methods yield good results only with small amounts of ammonia; with higher concentrations a titrimetric procedure is preferred.[71–75] The selection of the type of photometer depends on the range of concentration of nitrogen present.[76] The colour density of the solution after treatment with Nessler's reagent is dependent on the time after mixing of the reagent and the temperature at which the colour development is effected. The following times for colour development are preferred at the temperatures stated: 10°C., 30 to 50 min.; 15°C., 15 to 30 min.; 20°C., 10–20 min.; 25°C., 7–15 min.; 30°C., 5–10 min. The optical density of the solution is deeper with shorter wave-lengths and the relation between C, the concentration of nitrogen, and *d*, the optical density at 440 to 650 mμ is given by the equation:

$$d = kC + m$$

where k and m are constants which vary with wave-length. A S47 filter, $\lambda_{\text{min.}}$ 460 mμ, can be used with advantage.[77,78] The depth of colour after several minutes is generally found to be nearly independent of the method of mixing.[79] Nitrogen in organic compounds requires a Kjeldahl digestion before the Nessler treatment. Direct treatment of the digest with the reagent is common practice. In cases where mercuric sulphate is used as a catalyst in the digestion, the Nessler reagent can be produced *in situ* by the addition of potassium iodide to the neutralized digest. Sometimes a little gelatin, gum arabic or gum ghatti is added as a protective colloid for colour stability. Often distillation is necessary before addition of the reagent,[80–93] but direct addition of Nessler's solution is possible even when selenium oxychloride is used as a Kjeldahl catalyst.[94] The error due to turbidity, insufficient heating or escape of ammonia on prolonged heating is avoided by adding hydrogen peroxide, sometimes with trichloroacetic acid. Its use also avoids foaming.[95–99] A sealed-tube digestion of the sample with sulphuric acid at 450°C. before treatment with Nessler's reagent has also been recommended.[100] In certain cases, the sample is heated with lime, sodium hydroxide and sodium acetate: ammonia is evolved and the colour with Nessler's reagent is colorimetrically estimated.[101] The proper comparison colour tone for determining ammonia colorimetrically is obtained by the use of potassium chromate or dichromate or potassium chromate and cobalt nitrate.[102,103] There are several sources of error in the Nessler colorimetric estimation of nitrogen; some of these can be eliminated by proper conversion to ammonia and subsequent treatment with the reagent, by applying a blank correction, by avoiding the presence of ammonia in the reagents and apparatus, and by using the correct final alkali concentration.[104–106] Colorimetric estimation of ammonia using the Nessler reagent is applied to a wide variety of examples, such as ammonia of air, water, sewage, effluents, milk and several chemicals.[107–112] The conditions of the method have been described in several papers,[113–131] particularly those of Geiger[132] and Sijderius.[133]

TITRIMETRIC METHODS

Ammonia and alkaloids can be estimated by an electrometric titration.[134] A conductimetric titration for fixed ammonia,[135] ammonia and phosphoric acid fertilizers,[136,137] and for the ammonia content of ammino complexes[138] has been described. Steam distillation of ammonia followed by its absorption in acids and titration with standard alkali using Congo Red indicator gives a percentage relative error of ±0·1% even on a microscale.[139] In place of the usual indicators, a few drops of copper sulphate solution can be used; the appearance or disappearance of a blue colour is the end-point.[140] Some other indicators mentioned in the literature are anthocyanine, mixed methyl red–phenolphthalein, bromocresol, cochineal, sodium alizarinsulphonate, methyl red–bromothymol blue, bromocresol green either alone or with methyl red, and 4:4′-bis(*m*-tolyltriazeno)-2:2′-stilbenedisulphonate.[3,141–146]

Several authors have discussed the formol method which depends on the conversion of ammonia and formaldehyde to hexamethylenetetramine; the equivalent acid set free is then estimated.[147–154] Since visual titration fails in presence of hydrolysed protein compounds or when only traces of ammonia are present, recourse is had to an antimony electrode.[155] In a bromometric method, the solution of ammonium salt is added to an alkaline solution of bromine in potassium bromide, treated with hydrochloric acid and excess of arsenite solution, and the excess determined with standard bromine solution using indigo carmine as indicator.[156] The usual hypobromite titrimetry has been discussed by several authors; the method depends on the reaction:

$$2NH_3 + 3NaOBr \rightarrow 3NaBr + 3H_2O + N_2$$

The excess hypobromite is determined either iodimetrically or by means of naphthyl red which is decolorized by hypobromite, in a directly proportional manner.[157–159] Instead of hypobromite, hypochlorite can be used as an oxidizing agent for ammonia in a buffered solution; hypochlorite can be standardized against arsenious oxide with Bordeaux indicator.[160,161] In some cases, potassium bromide helps to control the reaction and serve as an indicator by yielding bromine as soon as all the ammonium ions have been oxidized; the solution must be buffered by disodium hydrogen phosphate.[162] The application of non-aqueous titration methods for the determination of inorganic salts, including those of ammonia, has been reported.[163] Very small amounts, less than 3 μg, of ammonia can be separated by the addition of sodium cobaltinitrite and potassium ions which serve to entrain all the ammonium ions; the precipitate is estimated by titration with potassium permanganate.[164] Other titrimetric methods discussed in the literature are of a general nature only.[165–174]

GASOMETRIC, GRAVIMETRIC AND POLAROGRAPHIC METHODS

The hypobromite reaction adapted to a gasometric method has been discussed earlier. Details of the method, the extent of its applicability and its limitations have been investigated by several authors.[175,176] To determine ammonia in presence of hydroxylamine, the latter is destroyed in a nitrometer by iodine in the presence of sodium acetate or potassium bicarbonate before the treatment with hypobromite; the evolved nitrogen then corresponds to ammonia alone.[12] In an adaptation of the Dumas method a measured volume of ammonia or a measured weight of its salt is oxidized with cupric oxide in a stream of carbon dioxide, and the evolved nitrogen as well as the volume of oxygen required to change the reduced copper back to copper oxide are determined.[177] By measuring the volume change after 'cracking' a certain volume of a gas, the ammonia content of that gas can be calculated.[178,179]

The chloroplatinate, the perchlorate and the cobaltinitrite methods usually employed for the gravimetric determination of ammonium ions have their limitations. Lithium or sodium tetraphenylboron has been found to give a precipitate of low solubility, but rubidium and cæsium ions also form insoluble salts with this reagent. A means of determining both ammonium and potassium in fertilizers has also been described.[180,181]

During the anodic polarographic oxidation of mercury in unbuffered potassium nitrate, the diffusion current is proportional to the ammonia concentration in the range of 1 to 15×10^{-4} molar.[182] An indirect polarographic method is based on precipitation with Nessler reagent and subsequent polarographic determination of mercury in the precipitate after conversion to the thiosulphate complex.[183] A rapid amperometric titration using hypobromite or hypochlorite has also been reported.[184,185]

OTHER METHODS

The amount of ammonia in a gas mixture is estimated by passing the gas through an absorbent such as an acid and measuring the electrical conductivity of the solution.[186–189] By comparing the resistance of two electrically heated wires, one surrounded by the gas to be analysed and the other by a reference gas, it is possible to determine ammonia in mixtures with nitrogen and hydrogen.[190] Determination of free ammonia in small amounts in fish meal can be carried out by an aeration method provided the temperature, pH and quantity of solution are maintained constant during aeration.[191] Free and saline ammonia in water can be distilled with steam on to a filter paper impregnated with manganous and silver nitrates, and the colour of the precipitated manganese dioxide and silver compared with a series of standard papers; after the determination of free and saline ammonia, 'organic ammonia' can be determined by adding alkali and some potassium permanganate and repeating the distillation.[192] From a gas mixture, ammonia and other absorbable components are estimated by placing a temperature-sensitive element, such as a mercury thermometer, irrigated with sulphuric acid in the gas stream and noting the heat of absorption.[193] The change in pH of an aqueous solution of a gas mixture can be correlated with its ammonia content.[194] The ammonia liberated from a Kjeldahl digest has been determined by a micro-diffusion method.[195,196] The ascending technique of paper chromatography using Nessler reagent gives a rough measure of the ammonia content of silage.[197] For the determination of ammonia in soaps, direct addition of alkali causes foaming, and the barium and calcium soaps may absorb some ammonia; hence they have to be decomposed by boiling with sulphuric acid and the extract added to the main filtrate before ammonia is distilled.[198–201] Several authors have also discussed the colorimetric, volumetric and other physical-chemical methods of analysis.[202–215]

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Determination of Amino-Nitrogen

Derivatives of ammonia as they are, the amino compounds have some of their analytical methods in common with those of ammonia. However, as a class they also have their own characteristic features. Some of these compounds are purely organic, but many of them form complexes with inorganic ions and compounds. The analysis of these complexes involves the decomposition, separation and analysis of the individual inorganic and organic components.

For the gasometric determination of amino-acids, the Van Slyke procedure is generally adopted. In the ninhydrin variation of the method, the amino acid is boiled in water with an excess of ninhydrin at a pH between 1 and 5; carbon dioxide is evolved quantitatively from two types of amino acids, $R{\cdot}CH(NH_2){\cdot}COOH$ and $R{\cdot}CH(NH{\cdot}CH_2R'){\cdot}COOH$. The carbon dioxide produced is transferred to the Van Slyke apparatus where it is absorbed in alkali; it is later regenerated by acidification and its pressure measured. The error due to volatile aldehydes is eliminated by the addition of hydrazine sulphate. When used in conjunction with the gasometric estimation of amino-groups by the nitrous acid method, this procedure can be adopted for the estimation of certain amino-acid mixtures. Another procedure is the determination of the ammonia evolved from primary α-amino-groups when amino-acids react with ninhydrin in boiling aqueous solution at pH 2·5; ninhydrin is removed as an insoluble derivative with hydrogen sulphide. The ninhydrin method has been adapted to the photometric determination of amino-nitrogen in several cases. The method is thus of wider applicability.[1–9]

Though not as specific as the ninhydrin procedure, the decomposition by nitrous acid is widely used for the determination of amino-nitrogen in amino-acids and primary aliphatic amines. The amine solution, in the absence of ammonia or urea, is acidified in the Van Slyke chamber and treated with sodium nitrite:

$$R{\cdot}NH_2 + HNO_2 \rightarrow ROH + H_2O + N_2$$

The nitrogen is extracted from the solution together with a much larger amount of nitric oxide produced by the decomposition of the nitrous acid. This mixture of gases is transferred to a Hempel pipette and freed from nitric oxide by treatment with alkaline permanganate. The pure nitrogen is returned to the Van Slyke chamber and its pressure is measured. Results from slowly reacting amines require some correction. The rate of reaction varies considerably with temperature. In fact, there is a primary reaction with a relatively rapid evolution of nitrogen, followed by a secondary reaction with a much slower evolution of nitrogen in which the rate is approximately constant for a limited period. In many cases the presence of iodide has been found beneficial. The method fails in the presence of tannin because, under the conditions of the Van Slyke determination, the tannin solution liberates a gas that is not absorbed in alkaline permanganate solution and hence increases the recorded amino-nitrogen value. If α-amino-nitrogen is to be determined in the filtrate from the protein precipitation, trichloroacetic acid must be used for the precipitation. Anomalous results are sometimes due to the reduction of nitrous acid itself. Modifications of the method have been evolved to study aromatic primary amines and aliphatic amino-groups. By the addition of mercuric chloride to the reaction mixture in the Van Slyke apparatus, practically the theoretical values are obtained for the amino-nitrogen content of glycines and peptides having a terminal glycyl group. Amides and urea or its derivatives have been analysed by suitable modifications. These and other features of the Van Slyke method have been discussed by several authors.[10–54]

Another gasometric procedure is the hypobromite method for urea and amino-nitrogen; no mercury is used.[55–57] On heating certain amino-acids with hydrochloric–nitric acid mixture, the amino groups are replaced by chlorine atoms; a gas, probably nitrogen or nitrous oxide, is evolved which is used for their estimation.[58–60]

Several titrimetric methods have been described: their details depend on the nature of the substance to be analysed. If there is interference from the presence of ammonia, as in the 'formol' titrations, it can be avoided by distilling the ammonia.[61] The end-points can be determined by suitable indicators or electrometrically.[62] One method consists in a titration with decinormal alcoholic hydrochloric acid after adding methyl acetate to 90% concentration and using naphthyl red as indicator.[63] Phenol red, thymol blue, neutral red and phenolphthalein have also been used as indicators.[64] Several other titrimetric methods have been discussed in the literature. The titrimetric method is the simplest of all procedures.[65–70] Samples of dried blood, fish meal, soybean meal, dried skim milk and a variety of other natural products can be analysed for their protein nitrogen by the Kjeldahl process.[71] If ammonium salts are present, the protein is precipitated as the tannate, washed free of ammonium salts and subjected to the Kjeldahl digestion.[72] Neither phosphotungstic acid nor phosphomolybdic acid is a satisfactory precipitant for peptones and certain other amino-acids.[73] There is also the Folin's colorimetric method for amino-acids, using β-naphthylaminesulphonic acid.[74–76] All primary, secondary and tertiary amines can be determined by titration in glacial acetic acid.[77] Formaldehyde renders non-volatile all the ammonia and the primary and secondary amines, but not the tertiary amine.[78] An azomethane-acidimetric method has been found suitable for the analysis of secondary plus tertiary amines.[79] For hexamethylenetetramine a titrimetric method which compared well with the Kjedlahl determination has been described.[80] Diazotization of aromatic amines and coupling them with suitable reagents produce colorations or dye-stuffs. By means of a colorimeter, the method is used for their estimation.[81]

Amide nitrogen is determined by heating the sample at 70°C. with hydrochloric acid or a concentrated hydrochloric–nitric acid mixture; the liberated nitrogen is collected in an azotometer.[82,83] For primary, secondary and tertiary amides, another method is based on reduction of the amides to the corresponding amine by means of lithium aluminium hydride. The amine formed is steam-distilled and then titrated with standard acid.[84]

Some of the amino-acids form insoluble or sparingly soluble copper salts, and the iodimetric method based on these gives good results.[85–87] Another simple procedure would be to determine the copper content of the complex with a flame photometer.[88] An adsorption method using three filters containing charcoal, Wofatit C, and Wofatit KS, respectively, has been described for the separation of amino-acid mixtures into aromatic, basic, acidic and neutral groups.[89] Application of quantitative paper chromatography for the assay of amino-acids involves the measurement of the maximum extension of a spot, produced with a suitable reagent, upon a chromatogram and measurement of the outline of a spot with a planimeter; logarithmic relationships of concentration to area exist in all cases, and 0·3 to 3·0 μg of amino-nitrogen is measurable. There are other chromatographic procedures.[90–94] Deamination of amino-acids occurs when they are treated with small amounts of alkaline sodium hypochlorite, and the evolved ammonia could be utilized for their determination.[95] Ammonia is also evolved from α-amino-acids when they are treated with *peri*-naphthindantrione or its *m*-nitro derivative.[96] Quantitative determination of proteins can be accomplished by a biuret method.[97] In many cases, a preliminary isolation of the amino-acids on an ion-exchange column leads to better results in any method adopted for their estimation.[98] Several authors have discussed the known procedures for primary, secondary and tertiary amines and ammonia in a mixture.[99,100] Variations, modifications and improvements of some of the above methods are frequently encountered in methods for the analysis of specific compounds or for the assay of general products.[101–112]

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Determination of the Oxides of Nitrogen

The main interest in the determination of the nitrogen oxides rests in their importance in air pollution and industrial poisoning by some of the extremely toxic oxides—nitric oxide, nitrogen dioxide, and its dimer, nitrogen tetroxide. Other frequently determined oxides are nitrous oxide, nitrogen sesquioxide and pentoxide.Two other oxides, nitrosyl peroxide, NO_3, and trinitrogen pentoxide, N_3O_5 are of academic interest only. Under ordinary conditions of temperature and pressure, the important oxides of nitrogen are gaseous and appropriate methods of collecting and handling the samples must be used. The samples are usually obtained from air, from atmospheres of mines or areas where explosives have been detonated or welding operations are being performed, or from others with the likely presence of one or more oxides of nitrogen. Sampling is based on either absorption or condensation.[1–6] In the absorption method, the air is passed at a suitable rate through a series of bubblers containing suitable absorbing solutions. In the condensation method, the air is passed through a series of traps which are immersed in progressively colder freezing mixtures; the traps may be preceded or followed by mechanical filters or scrubbers. When the sample is to be collected for analysis at a distant laboratory, special glass vacuum tube collectors may be used.[3]

NITROUS OXIDE

Combustion and reduction methods. Nitrous oxide is colourless and possesses anæsthetic properties. Ignition of this gas with hydrogen at bright red heat in a Drehschmidt platinum capillary tube and measurement of the decrease in volume is

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common analytical procedure: $N_2O + H_2 \rightarrow N_2 + H_2O$. Palladium is used as a catalyst. Carbon dioxide, if present, may interfere with the method owing to the following reaction[7–11]: $CO_2 + H_2 \rightarrow CO + H_2O$. In another variation carbon monoxide is substituted for hydrogen in order to eliminate interference by carbon dioxide. The reaction is: $N_2O + CO \rightarrow N_2 + CO_2$. The nitrous oxide content is estimated by direct measurement of the carbon dioxide produced or from the decrease in volume that results when the carbon dioxide is absorbed by a solid absorbent. When nitrous oxide is passed over a heated copper gauze, an equivalent amount of cupric oxide is formed: $N_2O + Cu \rightarrow CuO + N_2$. The copper oxide is subsequently reduced with hydrogen and the water formed is determined by absorption in a suitable desiccant. Thermal or catalytic decomposition of nitrous oxide over a heated platinum capillary produces equivalent amounts of nitrogen and oxygen. The increase in volume is equivalent to half the original amount of nitrous oxide: $N_2O \rightarrow N_2 + \frac{1}{2}O_2$. If higher oxides are present they are eliminated with the aid of concentrated sulphuric acid and the nitrous oxide frozen with liquid air before thermal decomposition.[12] In another method, manganous oxide reduces nitrous oxide at about 400°C.; the resulting higher oxides of manganese are determined iodimetrically.[23]

Absorption and fractional condensation methods. When a gaseous sample is cooled in liquid air, nitrous oxide and water vapour are condensed, and air and non-condensable impurities can be pumped off and measured. The sample is next raised to the temperature of solid carbon dioxide and acetone; the nitrous oxide that evaporates is pumped off and measured. The remaining water vapour is estimated by determining the vapour pressure after the residue is raised to room temperature. The method is simple and requires only about 30 min. for a complete analysis with a precision within $\pm 1\%$.[13–15] An absorption method with various absorbents that are specific for particular gases has been used for the analysis of a mixture of nitrous oxide with carbon monoxide, carbon dioxide, hydrogen, nitrogen and methane; the change in pressure after absorption is taken as a measure of the volume of the gas. There are provisions for combustion of certain constituents, wherever necessary, to convert them to forms suitable for absorption. Absorption of nitrous oxide in tap water at 0°C. has been employed as a simple method for the analysis of commercial nitrous oxide.[16] In another method chloroform is used to absorb the nitrous oxide.[17]

Physical methods. The mass spectrometer has proved particularly suitable for the analysis of small gas samples. The method has been applied to the determination of nitrous oxide in gases collected from soil samples, in the atmosphere, in blood, and in the pyrolytic products of organic compounds.[18] Special infra-red absorption spectrometers have been constructed for the estimation of nitrous oxide in air and blood. A sample of gas containing nitrous oxide will transmit less infra-red radiation than one containing only dry oxygen or air. The absorbed radiation will cause a rise in temperature, and a consequent increase in pressure proportional to the nitrous oxide content. The major infra-red absorption peaks of nitrous oxide are 590, 1285 and 2224 cm^{-1}. Another simple procedure for the assay of nitrous oxide is by means of a gas interferometer; results precise to within $\pm 0{\cdot}2\%$ have been obtained.[19] Of special interest for the analysis of nitrous oxide used in anæsthesia in admixture with oxygen and ether is the acoustic gas analyser, the principle of which is based on the considerable difference in the velocity of sound propagation for the component gases. Special measures are necessary if nitrogen is also present.[20] Anæsthetic mixtures are also analysed volumetrically.[21]

A katharometer based on the temperature variation of resistance in the presence of gases has been applied in the industrial analysis of a mixture containing nitrous oxide, carbon dioxide and methane.[22]

General information on the various factors which affect the analysis of nitrous oxide is to be found in several other papers.[24–33]

NITRIC OXIDE

Combustion methods. Nitric oxide is a colourless gas. When a mixture containing nitric oxide, carbon monoxide and hydrogen is burnt in a Drehschmidt platinum capillary heated to redness, nitrogen and carbon dioxide or moisture are formed: $2NO + 2CO \rightarrow 2CO_2 + N_2$; $2NO + 2H_2 \rightarrow 2H_2O + N_2$. Palladium is also a good catalyst. By placing a solution of potassium hydroxide over the mercury in a pipette connected to the platinum capillary, the carbon dioxide is immediately absorbed and the combustion proceeds quantitatively. The volume of nitrogen indicates the amount of nitric oxide. In the presence of nitrous oxide, the carbon dioxide need not be removed since the reduction in volume is equal to half the volume of nitric oxide. Decomposition of nitric oxide in contact with glowing copper also gives excellent results.[9,34,35] Catalytic hydrogenation of nitric oxide in presence of molybdenum or tungsten sulphide gives ammonia, and the analysis can be carried out colorimetrically. The method is useful for the removal of nitric oxide from coke-oven gas.[36]

Nitrometry. The use of a nitrometer is well known as a reliable method for the determination of nitric oxide. First designed by Lunge, the apparatus measures the volume of nitric oxide evolved from a reaction, and hence consists of two sections, a gas-generating unit and a measuring unit. It is assumed that if a solution of nitric acid, nitrous acid or a salt or ester of these acids is shaken with concentrated sulphuric acid and mercury, pure nitric oxide is produced.[37] Standardization of the apparatus is carried out by using a dry gas (air or nitrogen) or by the potassium nitrate method, manipulated in such a way that corrections for temperature and pressure are unnecessary. However, suitable corrections should be made for the solubility of the gas in the reagents used. Sulphuric acid at a concentration of 90% (v/v) offers the minimal solubility to the gas. Iron in any form in the sulphuric acid interferes and a modified Devarda method has been recommended in such cases.[38]

Absorption spectra. The infra-red absorption bands for pure nitric oxide in the gaseous state are at 1850 and 1925 cm.$^{-1}$ The liquid has two strong infra-red peaks at 1863 and 1770 cm.$^{-1}$ The infra-red method is particularly useful for the analysis of nitric oxide in admixture with other gases. Nitric oxide possesses a lone electron and exists as the dimer in the liquid state. The liquid has four strong Raman lines, at 1861, 262, 196, and 167 cm.$^{-1}$, which are exclusively due to the dimer.[39,40]

Chemical absorption, titrimetry and colorimetry. Most of the methods of analysis of nitric oxide are indirect and based on the estimation of some reaction product rather than of nitric oxide itself. The sample is absorbed in a medium which converts the nitric oxide into another active product which is then estimated. An oxidative absorption medium gives nitrites and/or nitrates; a reductive medium yields nitrogen or ammonia; and a complexing medium produces complex ions or molecules. These are then estimated by any of the well known methods such as colorimetry or titrimetry.[41] Nitric oxide is easily oxidized to nitrogen dioxide and nitrogen sesquioxide when mixed with air or oxygen. When this mixture is passed through a dilute solution of sodium or potassium hydroxide, nitrite and some nitrate are formed. By passing air into a mixture that is in contact with solid potash, only nitrite is formed. The decrease in volume is measured, four-fifths of which is due to the original nitric oxide content. It is apparent that excess of oxygen must be provided, the gases and potassium hydroxide must be anhydrous and carbon dioxide must be removed from the air. The use of monoethylamine is simpler owing to the insolubility of carbon dioxide in it. In another method, ethylaniline has been used for absorbing the gas, particularly in connection with the analysis in the nitrometer.[42] Anodic or other types of oxidation of nitric oxide to nitrogen dioxide and the estimation of the latter colorimetrically by the Griess reagent (sulphanilic acid plus α-naphthylamine) has been in use for the analysis of small quantities of nitric oxide in coal gas.[43,44] Conversion of nitric oxide to nitrogen dioxide can be tested by the Schuftan method using *m*-phenylenediamine; the method is generally employed for the analysis of nitrogen oxides (nitric oxide plus nitrogen dioxide) in coke-oven gas.[45–48] Oxidation of nitric oxide to nitrogen dioxide is also effected by passing the gas through an acidified solution of potassium permanganate; the nitrogen dioxide is absorbed in Griess reagent to give the coloration.[49] Hydrogen peroxide oxidizes gaseous nitric oxide to nitric acid. The acid may then be estimated by titration with standard alkali provided other acidic or basic gases are absent from the original gas. In such cases, potassium permanganate, acidic or alkaline, is preferable to hydrogen peroxide. The nitrate is determined by the usual methods or the residual permanganate is estimated by adding an excess of ferrous sulphate and back-titrating with permanganate.[50–52] Usually the permanganate oxidation is slow. Phosphoric acid is added to prevent precipitation of manganese oxides by the nitric oxide. The method is frequently used in relation to ammonia oxidation plants for the determination of nitric oxide and nitrogen dioxide. It is also stated that an acid solution of potassium bromate oxidizes nitric oxide quantitatively to nitric acid; the excess of bromate can be determined iodimetrically.[34,53] In a modification, potassium bromate is used to absorb nitric oxide in an Orsat gasometric apparatus and the difference in volumes obtained by the oxidation of nitric oxide to nitric acid is a measure of the amount of nitric oxide. If the nitrogen oxides in the waste gases of sulphuric acid production are passed over copper at 400–450°C., all the oxygen is removed and the nitrogen oxides are reduced to nitric oxide which can then be estimated.[54] Another oxidizing agent is potassium dichromate. But it is stated that oxidation with hydrogen peroxide and potassium dichromate is inferior to the permanganate method.[55] To determine nitric oxide in nitric acid, the sample is treated with perchloric acid and cerate solution, and the excess of cerate titrated with sodium oxalate using nitroferroin as indicator.[56] Formation of the brown-coloured nitrosyl ferrous salts, *e.g.*, $Fe(NO)SO_4$, is a well-known phenomenon observed when nitric oxide is passed through acidified ferrous sulphate or ferrous chloride solution. The complex is readily decomposed by heat and by other gases, particularly nitrous oxide. Alkaline sodium sulphite, preferably in the form of a paste with potassium hydroxide, absorbs nitric oxide to form sodium hyponitrososulphite, $Na_2N_2O_2SO_3$. The process can be adapted to a micro-method by holding the paste in the form of a bead on a platinum loop. It can be used with combustible gases such as hydrogen, acetylene and ethylene; in samples containing from 0 to 80% of nitric oxide, the average deviation is about 0·4% of the theoretical nitric oxide content. These processes are described in several papers.[57–60] The formation of nitrosylsulphuric acid when nitric oxide reacts with a solution containing 2 parts of concentrated nitric acid in 100 parts of 95% sulphuric acid is an excellent procedure: $2NO + HNO_3 + 3H_2SO_4 \rightarrow 3NO(OH)SO_3 + 2H_2O$. The nitrosylsulphuric acid can be treated with standard ferrous sulphate when its complex is formed.[60] Upon dilution, nitrosylsulphuric acid decomposes to nitrous acid, which can then be determined by any suitable method. The most frequently used and simplest method, particularly when very high accuracy is not required, is a direct titration with standard permanganate. For greater accuracy, the nitrosylsulphuric acid is added to an excess of standard permanganate solution, the excess is then treated with ferrous sulphate and the latter back-titrated with the standard permanganate. This procedure is necessary owing to the slowness of permanganate oxidation, and under these conditions the sharpness of the end-point is increased while the loss of nitrosylsulphuric acid by air oxidation is decreased.[61] If the end product of the absorption of nitric oxide is nitrous acid or nitrite, the latter can be estimated by a variety of methods specific for nitrous acid or nitrite. The most common colorimetric method is the Griess–Ilosvay reaction or its modifications, which involve the diazotization of an aniline compound such as sulphanilic acid and subsequent coupling with α-naphthylamine or other suitable amines or phenols.[62,63] Absorption in Griess–Ilosvay reagent is stated to be better than in *m*-phenylenediamine.[55] If the nitric oxide has been converted to nitrate, the phenolsulphonic acid method is generally applicable: the method depends on the nitration of a phenolic compound to complex but specific products. With phenoldisulphonic acid, as little as 0·05 mg. per litre of nitrate may be detected and measured at 410 mμ. An iodimetric method has been described for the analysis of nitric oxide in the gases evolved from smokeless powder; the presence of nitroglycerol volatilized from the powder does not affect the results.[64] During the oxidation of ammonia, analysis of nitric oxide in the products has been carried out by its heterogeneous reaction with oxygen on the wall of a vessel cooled in liquid air. No homogeneous reaction takes place under pressures of the order of 10^{-2} mm. of mercury, and excess of either nitric oxide or oxygen is ascertained by the fall in pressure on the addition of either oxygen or nitric oxide respectively.[65] There are several other general reviews on the analysis of nitric oxide under a variety of conditions.[66–71]

NITROGEN DIOXIDE AND NITROGEN TETROXIDE

Nitrogen dioxide (or 'peroxide') is a very poisonous gas with a characteristic odour. It contains an odd number of electrons, which accounts for both its reddish brown colour and its tendency to polymerize reversibly to colourless nitrogen tetroxide. There is also the dissociation equilibrium:

$$\underset{\text{brown}}{2NO_2} \xrightleftharpoons{<140^\circ\text{C.}} \underset{\text{colourless}}{N_2O_4}$$

$$\underset{\text{brown}}{2NO_2} \xrightleftharpoons{150\text{ to }620^\circ\text{C.}} \underset{\text{colourless}}{2NO + O_2}$$

The gas dissolves in alkali to give a mixture of nitrite and nitrate which respond to characteristic tests for these ions. Simple permanganate titration is usually adequate for the estimation. The important fact is that since only half the combined nitrogen dioxide reacts as nitrate or as nitrite, the results of determination must be multiplied by two. This applies to a large number of estimations involving this principle of absorption of nitrogen dioxide.[72–73] On the other hand, a method involving total reduction to ammonia by the Devarda or similar procedures gives the combined nitrogen.[74]

Physical methods of analysis. All physical methods suffer from the polymerization and dissociation effects in nitrogen dioxide. Any spectrum directly obtained on the gas will be a composite one. For u.v. absorption spectroscopy, it has been found that nitrogen tetroxide absorbs only up to 390 mμ and nitrogen dioxide absorbs in the region of 390 to 500 mμ. The other nitrogen oxides do not interfere. In a spectrophotometric method, nitrogen dioxide is measured at 394 mμ, nitrogen tetroxide at 240 mμ, and the total of the dioxide and the tetroxide at the isobestic point near 353 mμ. For pressures from 0 to 35 mm. of mercury, no pressure-broadening was observed. The coefficient of variation is ±9%, but this is acceptable in view of its high reactivity towards water and uncertainty in the degree of dissociation. The infra-red spectrum of nitrogen dioxide in the equilibrium mixture is rich in identifiable absorption bands. In the analysis of nitrogen dioxide in automobile exhaust gas, the optical density is measured at 6·15 μ. At the temperature used, the tetroxide can be assumed to be completely dissociated, and the effect of other oxides can be disregarded.[75] In using a mass spectrometer partial pressures of nitrogen dioxide between 15 and 200 microns (at which the equilibrium mixture consists of more than 99·9% of nitrogen dioxide) have to be used to get reproducible sensitivities for the principal mass peaks. Errors due to the interaction of nitrogen dioxide with traces of carbonaceous materials and adsorbed water can be eliminated by prolonged conditioning of the spectrometer by contact with nitrogen dioxide at 100 microns pressure. The accuracy of the results depends on the concentration of nitrogen dioxide and any other gases present. The method has been employed for the analysis of mixtures of helium, nitrogen, oxygen, hydrogen, water vapour, nitrogen peroxide, nitric oxide, nitrous oxide, carbon monoxide and carbon dioxide. All the components of the mixture may be determined.[76,77]

Titrimetry. The titrimetric methods are quite similar to those for nitric oxide. A method commonly used in acid plants is absorption in concentrated sulphuric acid; the reduction in volume is a measure of nitrogen dioxide. The nitrosylsulphuric acid formed may be titrated with potassium permanganate to give the amount of nitrogen dioxide. Better results are obtained by adding an excess of permanganate to the nitrosylsulphuric acid and determining the excess with ferrous sulphate or sodium oxalate or iodimetrically.[37,78,79] An oxidant better than permanganate is ceric nitrate: $NO_2 + Ce^{4+} + H_2O \rightarrow NO_3^- + Ce^{3+} + 2H^+$. An excess of ceric solution is added and then back-titrated with sodium oxalate. The end-point with nitroferroin, that is, nitro-*o*-phenanthroline ferrous sulphate, is very sharp.[56] Absorption of nitrogen dioxide in 3% hydrogen peroxide produces nitric acid which can be estimated acidimetrically using aqueous methyl red indicator. The method is superior to (*a*) the colorimetric methods with α-naphthylamine, with *p*-nitraniline and α-naphthol, or with iodo-starch paper, and to (*b*) the iodimetric determination; all of these methods respond also to nitrites or nitrous acid. Nitric oxide may easily be oxidized to nitrogen dioxide and then determined.[80,81] Alkaline hydrogen peroxide has also been used and the nitrate formed determined by the phenoldisulphonic acid method.[82]

Colorimetry. Most of the colorimetric procedures are in common with those for nitrous anhydride and nitrogen oxides. Since nitrogen dioxide dissolves in water, alkalis or potassium iodide solution to form a nitrite, it can be determined by the Griess–Ilosvay reagent containing sulphanilic acid and α-naphthylamine.[83] Owing to the instability of the complex dye, attention has been paid to finding better coupling agents. Some of them are: sulphanilamide or sulphanilic acid and *N*(α-naphthyl)ethylenediamine, preferably mixed in the dry form with tartaric acid instead of acetic acid, and 2-naphthylamine-6:8-disulphonic acid and α-naphthylamine. As permanent standards for colour comparison, aqueous solutions of basic fuchsin have been found suitable. A dyed set of cellophane strips has been used to match a series of colour standards corresponding to 5, 10, 20, 30, 40 or 50 p.p.m. of nitrogen dioxide in 50 ml. of air at 25°C. Only prolonged exposure to direct sunlight fades the colour of the dyed strips. Colour comparison is made spectrophotometrically. Other colorimetric methods for nitrogen dioxide use the following reagents: *m*-phenylenediamine in acetic acid; zinc iodide and starch solution; a combination of aurantia and neutral red, and safranine. These have been described in several papers.[84–90]

Other methods. The differential pressure between nitrogen dioxide and air or some other gas passing, under constant pressure, through a capillary or orifice is almost a linear function of the percentage of nitrogen dioxide in the gas, and the principle is employed in determining the composition of simple gas mixtures.[91] By the use of a photometer, coloured components of a mixture of nitrous gases have been determined.[92,93] Utilization of modulated light in photoelectric analyzers is another modification for the determination of nitrogen dioxide.[94] Analysis of dissolved oxides of nitrogen in nitric acid is a common necessity. One method is based on a titration with potassium permanganate.[95,96] Some other general methods and the modifications of those given above for the analysis of nitrogen dioxide are found in several other papers.[97–104]

NITROGEN SESQUIOXIDE, TRIOXIDE AND PENTOXIDE

Nitrogen sesquioxide or nitrous anhydride dissociates at ordinary temperature: $N_2O_3 \rightleftharpoons NO + NO_2$. Owing to this instability, it has the chemical properties of a mixture of nitric oxide and nitrogen dioxide, and the method of its determination is essentially that of such mixtures.[105] However, it is also claimed that nitrogen sesquioxide actually exists in the gaseous phase and that this molecule plays a most active part in the absorption processes.[106] The Devarda reduction and the distillation of ammonia so formed is one method used in its estimation.[107] The nitrous anhydride in nitrosylsulphuric acid is estimated by the permanganate method.[108]

Nitrogen pentoxide, or nitric anhydride, is also unstable and decomposes with violence: $2N_2O_5 \rightarrow 4NO_2 + O_2$. It dissolves readily in water to form nitric acid. Hence all methods suitable for determining nitric acid are applicable to this compound. Absorption bands occur at 5·8, 7·5, 8·0 and 13·5 μ, and such infra-red studies enable qualitative and quantitative analysis of nitrogen pentoxide to be carried out. Other methods have also been mentioned.[109]

Nitrogen trioxide, NO_3, also known as nitrosyl peroxide, is an intermediate product in the reaction between nitrogen pentoxide or nitrogen dioxide with ozone. It is also unstable: $2NO_3 \rightleftharpoons 2NO_2 + O_2$. Its detection can be achieved through its absorption spectra.[110]

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MIXTURES OF THE OXIDES OF NITROGEN

Nitrogen oxides. A mixture of nitric oxide, nitrogen dioxide and the oxides that exist in equilibrium with them, namely, nitrogen sesquioxide and tetroxide, is collectively known as nitrogen oxides or nitrous gases. For the determination of the total nitrogen content of such mixtures, the oxides are all absorbed in alkali and the nitrite formed is determined by standard colorimetric or titrimetric methods. Another simple procedure is the use of an interferometer or photoelectric colorimeter for nitrogen dioxide.[111–116] Absorption in alkaline hydrogen peroxide produces an equivalent amount of nitrate which can be determined colorimetrically using phenoldisulphonic acid or other suitable reagents. Acid hydrogen peroxide is very often found to be a better absorbent.[117,118] In another method the nitrate produced in alkaline hydrogen peroxide is reduced to ammonia and estimated with Nessler reagent.[119] The chloranil reaction and the polarographic method have also been employed.[120] Nitrogen sesquioxide in the form of a mixture of nitric oxide and nitrogen dioxide is important in the 'Chamber Process' for manufacturing sulphuric acid. Its analysis is based on the fact that nitrogen dioxide absorbs strongly in the ultra-violet and visible regions of the spectrum whereas nitric oxide is relatively weak in absorption; automatic photometers record the proportion of each oxide in the stack gases. There are also various other methods employing colorimetric, oxidimetric or other reagents.[121–131] For the analysis of 'smog' constituents the sample is first absorbed in a colorimetric reagent such as sulphanilic acid and *N*-(α-naphthyl)ethylenediamine, and the red colour produced is measured; this gives the amount of nitrogen dioxide. The nitric oxide is then oxidized to nitrogen dioxide by means of ozone, chlorine dioxide, potassium permanganate or hydrogen peroxide, followed by a colorimetric estimation of the generated nitrate by means of phenoldisulphonic acid; nitrites which may also be formed can be determined satisfactorily by various methods.[132] For a mixture of nitrogen dioxide and nitric oxide, all of the nitrogen dioxide and part of the nitric oxide (equivalent to nitrogen sesquioxide) is first absorbed in alkali and the escaping nitric oxide is shaken with hydrogen peroxide and oxygen: the nitric acid so formed is estimated by usual methods. In the first fraction, excess alkali is titrated with sulphuric acid and subsequently with potassium permanganate to determine the nitrites. From the results, a complete analysis is possible.[133] In another method nitrous anhydride is absorbed in concentrated sulphuric acid and the reduction in volume measured over mercury; a portion of the residual nitric oxide is analysed by oxidation with potassium bromate solution.[134] Absorption of nitric oxide and nitrogen dioxide in 95% sulphuric acid gives nitric acid and nitrosylsulphuric acid. Total nitrogen in the solution can be determined with a nitrometer and the nitrosylsulphuric acid by titration with potassium permanganate.[135] In the Schuftan method, the nitric oxide is oxidized to nitrogen dioxide and estimated colorimetrically by means of *m*-phenylenediamine.[136] After the oxidation of nitric oxide the Griess–Ilosvay reagent can be employed as a colorimetric reagent.[137,138] Another method depends on the addition of an excess of oxygen, followed by freezing out the nitrogen dioxide and removal of excess of oxygen. The consumption of oxygen is a measure of the nitric oxide present. The nitrogen dioxide can also be determined by titration with potassium permanganate.[139] The permanganate–ferrous sulphate method can be employed for the estimation of a mixture of nitric oxide and nitrogen dioxide. But the absorption of these gases in permanganate, hydrogen peroxide or sodium hypochlorite is never quantitative.[140] The permanganate–ferrous sulphate method can also be adapted to be followed colorimetrically as has been carried out for the determination of residual nitrogen oxides in spent sulphuric acid.[141] For a rapid but approximate analysis of nitrogen oxides, the sample is injected into a solid absorbent column of silica gel and a colour is developed on the column by means of a diphenylamine–sulphuric acid solution. The accuracy is only 20% over the range 1 to 50 p.p.m., but the analysis is complete in about 5 minutes and can be performed outside the laboratory.[142] Silica gel containing acidified potassium dichromate is also a good absorbent: while it is absorbing

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nitrogen oxides, the orange-yellow colour turns green and this colour can be compared with standards.[143] Other features of the analysis of nitrous gases have been discussed by several authors.[144,145]

Nitrous oxide, nitric oxide, and nitrogen. The nitrous oxide and nitric oxide are absorbed in acidified permanganate and thereby oxidized to nitrate. In the absence of nitrogen dioxide, the solution is titrated with ferrous sulphate until the characteristic reddish brown colour of the nitrosyl-ferrous complex is obtained. If nitrogen dioxide is present, spectrophotometry in the visible and infra-red regions is suitable.[146] An infra-red method has been developed for samples containing nitrous oxide, nitric oxide, carbon monoxide, nitrogen and hydrogen.[147]

Nitrous oxide, nitric oxide, nitrogen dioxide, and nitrogen. The reaction of nitrogen oxides with finely divided nickel at 800°C. is employed in one method. Under these conditions, the oxides are rapidly reduced to nitrogen with the formation of an equivalent amount of nickel oxide. The nitrogen produced may be determined volumetrically, and the oxygen may be determined by the volume of hydrogen required for the reduction of the nickel oxide. If nitrogen dioxide is present, it is first separated by condensation at −80°C. and then estimated separately by reduction over nickel. In a chemical method, the total of nitric oxide and nitrogen dioxide in one portion of the sample is oxidized by hydrogen peroxide to nitric acid which is determined by titration with alkali. A second portion is absorbed in a solution of nitric acid and sodium sulphate in sulphuric acid and then titrated with permanganate; the residual gas is passed first through potassium hydroxide solution to absorb carbon dioxide, then through alkaline pyrogallol to absorb oxygen, and the nitrous oxides in the residual gas is determined by combustion with hydrogen; the nitrogen is determined by difference.[148] Coarsely powdered caustic soda absorbs nitrogen dioxide but not nitric oxide; the total nitrogen absorbed is determined by the Devarda method and the nitrite by permanganate titration; the residual gas can be chilled by liquid air to condense the nitrous oxide to a solid and the nitric oxide determined by the ferrous sulphate method or by the alkaline sulphite method.[149] Klemenc has described four general methods for the analysis of a gaseous mixture containing nitrogen, nitric oxide, nitrogen dioxide, and their polymers.[150] For the analysis of a mixture containing nitrogen, nitrous oxide, nitric oxide, nitrogen dioxide, carbon monoxide, carbon dioxide and oxygen, the gas is first passed through an absorption train of acidified ferrous sulphate, acidified potassium permanganate, potassium hydroxide solution, alkaline pyrogallol and ammoniacal cuprous chloride, which removes respectively nitric oxide, nitrogen dioxide, carbon dioxide, oxygen and carbon monoxide. Hydrogen is added to the residual nitrous oxide and nitrogen, and passed over heated platinum to determine nitrous oxide; hydrogen is removed as water vapour by cupric oxide at 300°C., and nitrogen is obtained by difference. The results are precise to ±1%.[151]

Miscellaneous mixtures. The use of a mass spectrometer is the best method for rapid analysis of mixtures containing all the oxides of nitrogen. In combination with ultra-violet spectroscopy, the mass spectrometer allows separation and determination of mixtures of nitric oxide, nitrous oxide, nitrogen, carbon monoxide, carbon dioxide, oxygen and hydrogen.[152] Another physical method for the separation and determination of the oxide mixture is by means of gas chromatography. Silica gel cooled in solid carbon dioxide and acetone is used as the adsorbent, and helium as the carrier gas. Separation and estimation of such binary mixtures as nitrous oxide and carbon dioxide, nitrogen and oxygen, nitric oxide and carbon monoxide, as well as of more complicated mixtures such as nitrogen, nitrous oxide, nitric oxide, carbon monoxide and carbon dioxide can be readily accomplished; thermal conductivity cells are used as detectors.[153] If the column is made of sections of silica gel, iodine pentoxide, silver powder and a final layer of silica gel, all maintained at 150°C., complicated mixtures of nitrogen, nitrous oxide, nitric oxide, carbon monoxide and carbon dioxide can be analysed. Nitric oxide and carbon monoxide are oxidized to nitrogen dioxide and carbon dioxide respectively. Thus nitric oxide is not determined directly.[154,155] Nitric oxide in admixture with hydrogen or nitrogen can be absorbed in solid

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caustic potash and determined by the difference in volume. In ammonia–nitrous oxide mixtures, ammonia is absorbed in chloroacetic acid and nitrous oxide determined.[156] Milligan has proposed a complete scheme for the quantitative determination of reduction products of free nitric acid, namely, nitrogen dioxide, nitric oxide, nitrous oxide, nitrous acid, hydroxylamine, hydrazine and ammonia.[157] There are also other comments on the analysis of a mixture of nitrogen, nitric oxide, nitrogen dioxide, nitrogen tetroxide and nitrous anhydride.[150] A method depending on the change in the electrical conductivity of a solution has been devised for the determination of nitrogen oxides.[158] All oxides of nitrogen except nitrous oxide are absorbed in acid hydrogen peroxide with the formation of nitrate which can be estimated colorimetrically with phenoldisulphonic acid.[159] There are also several general schemes using one or more of the above procedures for the analysis of individual oxides of nitrogen or their mixtures, alone or in presence of other gaseous components.[160–200]

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Determination of the Oxyacids of Nitrogen and their Salts and Derivatives

The two important oxyacids of nitrogen are nitric and nitrous acids. Of these nitrous acid is unstable and is known only in dilute aqueous solution, but the nitrites are quite stable. The other oxyacids are hyponitrous acid, $H_2N_2O_2$, hydronitrous acid, $H_4N_2O_4$, peroxynitric acid, HNO_4, and pernitrous acid, $HO{\cdot}O{\cdot}NO$. The last four have no significant commercial interest.

NITRIC ACID

Pure nitric acid is a colourless liquid, but undergoes a reversible decomposition on exposure to light: $2HNO_3 \rightleftharpoons 2NO_2 + H_2O + \frac{1}{2}O_2$. The characteristic yellow-to-red colour of the acid is due to the dissolved nitrogen dioxide. Red fuming nitric acid is saturated with nitrogen dioxide and contains from 6·5 to 22·0% by weight of dissolved oxides of nitrogen and total nitrogen equivalent to over 100% of nitric acid. Chemically, nitric acid behaves both as an acid and as an oxidizing agent, and also undergoes substitution reactions. Determination of nitric acid with standard alkali is based on its strong acid nature. Another titrimetric method for nitric acid is based on its oxidizing power. Fuming nitric acid containing nitrogen dioxide is especially rapid in its oxidizing action. The analyses with reducing agents, such as ferrous sulphate, are based on this property. Many of the colorimetric methods are based on

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substitution reactions and are of importance in the analysis of nitro and nitrate groups.

In dealing with nitric acid special precautions are necessary during sampling, weighing and dissolving owing to its volatility and reactivity. Titration with standard alkali gives the total acidity, part of which corresponds to impurities such as sulphuric and hydrochloric acids as well as lower oxides of nitrogen. In presence of sulphuric acid, nitric acid can be electrolytically reduced to ammonia and the equivalent decrease in acidity determined by titration.[1,2] In a mixture of sulphuric and nitric acids, addition of excess of barium carbonate precipitates barium sulphate and the filtrate will contain barium equivalent to the amount of nitric acid; this barium can be estimated in the usual way.[3] In another method, the mixed acid is passed over partially oxidized copper at red heat when nitrogen, water vapour and sulphur dioxide are formed; these gases are estimated after separation by condensation and fractional distillation.[4] A simple conductimetric titration of the mixed acid with barium acetate gives the amount of sulphuric acid, and the total acid is determined titrimetrically.[5–7] In organic solvents, nitric acid can be titrated with *n*-amylamine dissolved in dibutylcarbitol to a bromophenol blue end-point or with sodium sulphocyanide as indicator.[8] The ferrous sulphate method is applicable in the presence of sulphuric, phosphoric, or arsenic acid; nitrites up to 50% would not cause serious interferences, but oxidizing agents and halides do so. The nitric acid is treated with an excess of ferrous sulphate and the excess titrated with potassium permanganate. In this way, 0·15 to 0·7% of nitric acid in sulphuric acid can be determined with a coefficient of variation of ± 5%.[9] This titration can also be followed electrometrically.[10] Many of the analytical methods for nitric acid are common with those for nitrates, and hence are discussed under nitrates. Certain methods, said to be almost specific for nitric acid, are dependent on unusual properties such as those of an ether solution,[11,12] its action on certain electrodes[13] or the conductivity of its barium salt.[14]

NITRATES

Nitrites interfere with the estimation of nitrates. They are therefore eliminated by any of the following methods: (*a*) repeated evaporation with acetic acid, (*b*) boiling with urea in acid solution, (*c*) boiling with sulphamic acid, ammonium sulphamate or ammonium chloride, (*d*) treatment with hydrazine or hydroxylamine, and (*e*) treatment with sodium azide. After the elimination of nitrites, nitrate can be exclusively estimated by any of the normal methods. For example, low concentrations of sodium nitrate in sodium nitrite are determined after the elimination of the nitrite; nitrate can then be determined by a method involving nitration of nitrobenzene and causing the resulting dinitrobenzene to react with acetone and alkali to produce a colour.[15–19]

Titrimetry

Nitrates are easily reduced to ammonia when the sample is treated with Devarda's alloy, aluminium, iron, zinc–copper couple, copper–magnesium, ferrous sulphate or ferrous hydroxide in an alkaline solution. The ammonia is distilled as in the Kjeldahl method, collected in standard acid and estimated by methods described earlier.[20–34] The Kjeldahl treatment of nitrates with phenolsulphonic acid and potassium sulphate, if properly carried out, gives quantitative results. Tannin (of leather) and certain other natural products interfere in the analysis.[35–38] The use of sodium thiosulphate and thiosalicylic acid in the Kjeldahl digestion is also suitable. The quantity of salicylic acid used is more important than the relative merits of zinc or thiosulphate used for the reduction.[39,40] When zinc is used as reducing agent incomplete reduction of nitrate has been shown to be due to the presence of mercury which forms a film of hydride around the zinc. This interference can be prevented by adding an extra quantity of alkali metal sulphite. The use of chromo-sulphuric acid is very efficient in such cases.[41] Nitrates can be determined by treatment with concentrated sulphuric acid and titration with ferrous sulphate; nitrosulphuric acid, ferric sulphate and water are the products formed.[42] Nitrates are reduced by formic acid in the presence of sulphuric acid to nitrosylsulphuric acid which can be titrated with iodine or potassium permanganate.[43] Ferrous sulphate reduces nitrates to nitric oxide in an acid solution. Ammonium molybdate catalyses the reaction. The method has been applied to the analysis of fertilizers, meat pickle salts, and spent or mixed acids. The excess of ferrous sulphate can be estimated by titration with potassium permanganate.[44,45] Nitrates and nitrate esters such as nitrocellulose, nitroglycerol, and pentaerythritol tetranitrate are determined by a direct titration in sulphuric acid at a temperature below 15°C. with ferrous sulphate solution to a dead-stop end-point with 15 mv. applied between platinum electrodes.[46] In alkaline solution, nitrates are reduced to ammonia when treated with ferrous sulphate. Silver sulphate catalyses this reduction. The ammonia is distilled off and estimated. Or, when the reduction is complete, the solution is acidified and the excess of ferrous sulphate is titrated with potassium permanganate. In view of the possible atmospheric oxidation of ferrous salts, particularly in the alkaline media, it is necessary to apply a correction.[47] An inorganic nitrate can be analysed for its nitrogen content by heating with sodium carbonate followed by heating with an excess of a mixture of dry lime and sulphur and by titrating the evolved ammonia.[48] In the stannometric method the nitrate is first reduced with ferrous sulphate in alkaline solution containing silverdiammine sulphate, the ammonia is boiled off, the solution is acidified with concentrated hydrochloric acid and the ferric iron is titrated with standard stannous chloride; the end-point is observed potentiometrically or by using thiocyanate as indicator. In the latter case, addition of disodium hydrogen phosphate and ammonium molybdate at the end-point improves the titration.[49] The nitrates in crops can be reduced to ammonia by *ferrum redactum* and then the usual Kjeldahl method is applied for total nitrogen.[50] Another reducing agent is sodium sulphite, chromic sulphate, mercuric oxide and zinc[8]. Titanous salts reduce aliphatic nitrates in the hot and the excess is estimated by titration against ferric solution with methylene blue as indicator; results nearer to the theoretical are, however, obtained only if it is assumed that each nitro-group is equivalent to 7·5 titanous ions (instead of 8).[51] In another method the reaction between sulphamic acid and nitric acid is used in the determination of nitrates by titration of the excess of sulphamic acid with sodium nitrite solution using starch-iodide as external indicator.[52]

Gravimetry

Nitron, $C_{20}H_{16}N_4$, which is 1:4-diphenyl-3:5-endanilo-4:5-dihydro-1:2:4-triazole, is the best known gravimetric reagent for nitrates. Of the interfering ions, bromides are removed by adding chlorine water, iodides by boiling with potassium iodate, and nitrites and chromates by reduction with hydrazine sulphate. Large quantities of chlorides necessitate a correction.[53] 'Fornitral' is said to be a gravimetric reagent superior to nitron; the precipitate when dried at 110°C. contains 16·8% of nitric acid.[54] Other sensitive gravimetric reagents for nitric acid and nitrates are di(α-naphthylmethyl)amine acetate and di*cyclo*hexylphthalates. With the former reagent, phosphoric and sulphuric acids do not interfere, but other minerals acids should be absent.[55,56]

Nitrometry

Nitric oxide is evolved from nitrates or organic nitrocompounds undergoing reactions of the following type: $2KNO_3 + 4H_2SO_4 + 3Hg \rightarrow H_2SO_4 + 4H_2O + 2NO + 3HgSO_4$. Nitric oxide is also produced when acidified nitrates are reduced by ferrous chloride. The gas is measured in an azotometer. Nitrites, if present, should initially be decomposed to nitrogen by boiling with urea in acid solutions.[57–62] Nitrometric analyses have been extended to the nitrosamines, nitramines, and alkyl nitrates.[63,64]

Colorimetry and Spectrometry

Nitration of phenols, reaction with amines, and reduction to nitrites followed by the diazo reaction are some of the general methods used in the colorimetric estimation of nitrates. Phenoldisulphonic acid gives a yellow nitration product, which is identified as 6-nitro-2:4-phenoldisulphonic acid; the colour is intensified when alkali is added. Chlorides, carbonates and organic matter must be absent, and nitrites in large amounts should be destroyed or a correction applied for them. The method is suitable for nitrates in water and soils. Application of alkaline sodium potassium tartrate solution to hard water has been recommended for the prevention of interference from calcium and magnesium salts.[65–67] Pyrogallol, or its sulphonic acid, in sulphuric acid gives a series of coloured products. Sulphosalicylic acid is better than phenoldisulphonic acid and can be used to determine nitric acid in chromic acid anhydride.[68] Moreover, mono-, di- and tri-nitrophenols follow Beer's law only within a very narrow interval, thus discrediting the use of the phenolsulphonic acids for the estimation of nitrates.[69] 3:4-Xylenol is nitrated to 6-nitro-3:4-xylenol when treated with nitric acid or nitrates acidified with concentrated sulphuric acid. The nitro-compound is steam-distilled into alkali when a deeply coloured solution is formed. Chromotropic acid, 4:5-dihydroxy-2:7-naphthalenedisulphonic acid, produces a yellow colour with nitrates in presence of concentrated sulphuric acid; nitrites and ferric ions do not interfere.[70] Nitration of 4-hydroxy-1:4-dimethylbenzene also gives a coloured product. The method is used to estimate the nitrates in salted meat in presence of nitrite.[71] Nitrates in boiler water are determined by the colour developed with brucine in sulphuric acid. Nitrites and chlorides interfere. In more dilute acids, only nitrites are sensitive to this reagent and this phenomenon can be utilized for nitrate estimation; both nitrate and nitrite can be determined together, from which the concentration of the nitrate can be deduced. Reduced strychnine reacts with nitrates in the presence of sulphuric acid to produce a rose-coloured solution. Chlorides do not interfere but oxidizing agents give positive tests with the reagent. Nitrites react with the reagent before the addition of the acid, and a correction is therefore necessary. Michler's ketone, 4:4′-bis(dimethylamino)-benzophenone, in sulphuric acid produces a yellow colour with organic and inorganic nitrates, but not with chlorates, iodates, persulphates or peroxides; nitrites, however give a positive test. Nitrates in drinking water may be estimated from the blue colour produced on the addition of diphenylamine sulphate to a sulphuric acid solution.[72] Under the influence of ultra-violet radiation, diphenylamine and nitrate (concentrated sulphuric acid is not required) react to form a yellow-coloured product. The method can be used in conjunction with paper chromatography. Nitrites are produced on the reduction of nitrates with zinc in an acid solution; the nitrite diazotizes aniline, which then couples with α-naphthylamine to form a red colour. The intensity of this colour follows Beer's law, and the sensitivity is 0·01 μg per ml.[70] Nitrates are also reduced by zinc dust and manganous sulphate. The reduction is carried out in the presence of α-naphthylamine, sulphanilic acid and acetic acid, and the depth of colour of the filtrate can be measured in a spectrophotometer at 520 mμ or in a filter photometer with a green filter.[73] Other colorimetric methods involve the use of *m*-diaminophenol, pentachlorophenol (chloranil), and 4-aminobenzenesulphonic acid.[74–76] Nitrates react with ferrous sulphate–sulphuric acid reagent to form a red-purple colour, the optical density of which is determined at 525 mμ. The method is applicable to the analysis of water and spent sulphuric acid. Addition of ferrous sulphate and a bisulphite to a mixture of nitrate and sulphuric acid also produces a colour which can be compared with standards.[77–80] From the ultra-violet absorption at 210 or 220 mμ of a solution of nitrates in dilute perchloric acid, nitrates have been estimated to a very high precision. Quantitative analysis of a nitric–sulphuric acid mixture has also been accomplished by comparing photometrically the Raman spectra; the line 1368 cm.^{-1} is specially suitable.[81,82]

Other Methods

The surface tension of 85 to 100% nitric acid is found to be a linear function of the concentration; the principle is used in the analysis of the acid.[83] Nitric acid, nitrates and a large number of anions and cations have been separated chromatographically by use of paper impregnated with alumina and developed with water.[84,85] Polarographic methods, though not emphasised in the literature, have also been mentioned in some papers.[86,87] Polarographic reduction of nitrates (and nitrites) occurs only in the presence of bivalent and trivalent cations, particularly La^{3+}, Ce^{3+} and UO_2^{2+} cations. Anions affect the half-wave potential considerably. Nitrites, if present, can be eliminated by boiling with sulphamic acid or sodium azide, so that nitrate alone can be determined.[88–93]

Modifications to these and other methods and reviews on groups of them are also to be found.[8,94–101]

NITROUS ACID AND NITRITES

Nitrous acid is stable only in cold, dilute, aqueous solutions. It decomposes thus: $3HNO_2 \rightleftharpoons H_2O + HNO_3 + 2NO$. Strong oxidizing agents oxidize it to nitric acid, and it can also be reduced to nitric oxide, hydroxylamine, hyponitrous acid and ammonia, each step involving two electrons.

A gravimetric method for determining nitrous acid is based on the reaction: $AgBrO_3 + 3HNO_2 \rightarrow 3HNO_3 + AgBr \downarrow$.

For the analysis of small amounts of nitrous acid, colorimetric methods are employed, which are the same as those for nitric oxide and nitrite. Titrimetrically nitrous acid is estimated cerimetrically or permanganometrically.[102] Most of these methods are directly applicable to nitrites.

Titrimetry

In warm acid solution, potassium permanganate oxidizes nitrites to nitrates: $5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$. The nitrite preferably is added from a burette into acidified permanganate. The end-point can be determined potentiometrically. Even with this Lunge modification, the results are not particularly accurate since the nitrite does not react instantaneously with the permanganate and losses due to volatilization and decomposition are not completely eliminated. In another modification, nitrite is mixed with an excess of permanganate and the excess of the latter back-titrated iodimetrically or by other means. Fluorides interfere in the titration.[103–112] Better results are obtained by using phosphoric acid instead of sulphuric acid.[113] If hyponitrites are present, they are destroyed by boiling before the nitrite is estimated permanganometrically or in the nitrometer.[114] Hyponitrites can be estimated separately volumetrically with potassium thiocyanate; nitrites and nitrates do not interfere, but both nitrite and hyponitrite give insoluble silver salts.[115] The nitrites of Werner complexes such as a nitrito-cobalt complex are better oxidized by acidified potassium dichromate under pressure and at 110°C. rather than by permanganate.[116] Bell recommends *p*-nitraniline as a primary standard for sodium nitrite. This is dissolved in hydrochloric acid and titrated against sodium nitrite from a burette using starch-iodide paper to indicate the end-point.[117] In similar titrations against amino compounds, biphenyl azo dyes such as tropæolin or metanyl yellow can be used as indicators.[118] An iodimetric method, applicable to both organic and inorganic nitrite, is based on the reaction: $NO_2^- + I^- + 2H^+ \rightarrow NO + I + H_2O$. The liberated iodine is titrated with standard sodium thiosulphate.[103,119–127] An atmosphere of carbon dioxide is maintained in the reaction flask. Measurement of the potential of an iodine–iodide electrode serves to determine the amount of iodine liberated.[128] Nitrites are oxidized by bromine in pyridine solution, and the excess of bromine determined by adding potassium iodide and titrating the liberated iodine with sodium thiosulphate.[129] Nitrites are also oxidized by bromate in presence of hydrochloric acid or a bromide and sulphuric acid; the liberated bromine is removed by boiling and the excess of bromate back-titrated iodimetrically[130] against arsenious acid or against potassium antimonyl tartrate.[131] Trivalent manganese stabilized with pyrophosphate can be used for the titration of nitrites with diphenylaminesulphonate as indicator.[132] Dilute nitrous acid reduces chlorates to chloride; this chloride is treated with an excess of silver nitrate, and after removing the precipitated silver chloride, the excess of silver nitrate in the filtrate is titrated with ammonium thiocyanate using ferric alum indicator.[133,134] Ceric sulphate has been employed for the titration of nitrites with erioglaucine as indicator.[135,136] Nitrites are also oxidized by chloramine-*T*, the end-point being detected potentiometrically.[137] If hypochlorite is the oxidant, the excess is titrated with potassium iodide solution.[138] Another oxidimetric titrant is the bivalent silver complex with α-α'-bipyridyl, $[Ag(C_{10}H_8N_2)_2]^{++}$; the colour change is from red to colourless.[139] By heating nitrites with zinc and ferrous sulphate in the presence of sodium carbonate, ammonia is formed and can be estimated as in the Kjeldahl process. Ferrous hydroxide alone will reduce nitrites (and also nitrates) to ammonia in most cases.[25,140] If zinc is replaced by *d*-glucose, only nitrite is reduced but not the nitrate.[141] A preliminary reduction with titanous chloride followed by zinc dust in conjunction with platinum chloride catalyst prior to the Kjeldahl digestion is found to give accurate results for nitrites, including 'highly nitrated' derivatives.[142] By adding nitrites to an excess of acidified hydrazine and back-titrating the excess hydrazine with iodine solution, nitrites can be estimated even in the presence of nitrates or chlorides. An acidimetric method using hydrazine has also been described.[143] When an excess of hydroxylamine reacts with nitrite, the excess can be back-titrated with sodium hydroxide using methylene blue–phenol red indicator.[144] The reaction of nitrite with sulphamic acid can be made the basis of a titrimetric procedure, with sulphanilamide and α-naphthylamine reagent as an external indicator.[145] An indirect method of estimating sodium nitrite in nitrates is based on the formation of ethyl nitrite in the reaction of sodium nitrite with ethyl alcohol and sulphuric acid: the excess sulphuric acid is then titrated.[45]

Nitrometry. Nitrites react with sulphamate or urea in acid solution liberating nitrogen: $HNO_2 + HSO_3.NH_2 \rightarrow H_2SO_4 + H_2O + N_2$; and $2HNO_2 + CO(NH_2)_2 \rightarrow 3H_2O + CO_2 + 2N_2$. The method suffers from the fact the evolved gas contains some of the decomposition products of nitrous acid itself.[59,146,147] For example, in the reaction between sodium nitrite and sulphamic acid, as much as 10% of the gas evolved is a mixture of nitric oxide and nitrogen dioxide. Hence the experimental value is usually multiplied by a factor of 0·9746 to obtain the correct results. However, the nitrogen oxides can be absorbed in alkaline potassium permanganate or sodium sulphite and estimated separately.[148] Some other nitrometer methods have also been mentioned.[149]

Colorimetry. The diazonium salts, produced by the reaction of nitrites with acidified aromatic primary amines, couple with a variety of aromatic phenols and amines to produce the azo colour which is suitable for either visual or photometric measurements. The Griess reaction with sulphanilic acid and α-naphthylamine is the most popular owing to its sensitivity, adherence to Beer's law over a wide range of concentration, low dependence on pH, its short reaction time and other experimental conditions. Its chief drawback is the relatively short period of colour stability. In the widely used method, sulphanilic acid is diazotized with the nitrite in acetic or hydrochloric acid media, and is then coupled with phenols or amines; phenol, indole, α-naphthylamine, dimethyl-α-naphthylamine, dimethylaniline, *N*-(α-naphthyl)ethylenediamine, β-naphthol and pyrocatechol have been used for this purpose, but α-naphthylamine is the most common.[150–169] Interference from hydrogen sulphide is overcome by adding cadmium carbonate or zinc carbonate suspensions.[170–172] Addition of tartaric acid eliminates interference from several ions.[173] Sometimes esterification of nitrous acid followed by the colorimetric analysis with Griess reaction is found to be an advantage.[174] Sulphanilic acid may be substituted by *o*-aminobenzoic acid,[175] novocaine or atoxycocaine,[176] or sulphanilamide.[177–179] Hydroxylamine and oximes can be determined by this method provided they are first oxidized to nitric acid by mixing them with sulphanilic acid, acetic acid and iodine.[180] Dimethylaniline or α-naphthylamine gives the yellow colour of their *p*-nitroso-derivatives when they are treated with nitrites or nitrous acid. Nitrates do not interfere. This colorimetric method can detect 1 p.p.m. of nitrite. Pyrogallol, pyrocatechol, hydroquinol, orcinol and resorcinol also produce similar coloration or fluorescence.[181–185] Sodium nitrosonaphtholsulphonate in acid solution reacts with nitrites to give a dye, and this is estimated spectrophotometrically in the alkaline solution.[186] Acidified nitrites liberate iodine from potassium, zinc or cadmium iodides and after addition of starch, the blue colour of the starch-iodine complex is employed for a rough colorimetric estimation of nitrites.[187] Nitrites in water, soil extracts and other aqueous solutions may also be estimated by brucine hydrochloride or hydrostrychnine.[188] Nitrites are oxidized to nitrates by hydrogen peroxide and potassium permanganate; the nitrate is then colorimetrically estimated by the usual methods. The end-points in the oxidation can also be determined potentiometrically.[189–191] Some other colour reactions which have been employed for colorimetric estimation of nitrites are: blue coloration with neutral red in phosphoric acid[66,192]; yellow-green to red colour with acridine dyestuffs in hydrochloric acid[193]; diazotization of sulphanilic acid or sulphanilamide[194,195]; green to yellow colour with Erioanthracene Pure Blue 2GL[196,197]; decolorization of methyl red or methyl orange[198]; reaction with violuric acid[199]; violet to blue colour change of gentian violet[200]; and colour reactions with *o*-aminobenzalphenylhydrazone,[201] alcoholic α-naphthylamine hydrochloride[202] and *m*-phenylenediamine hydrochloride.[203] Nitrites can be separated from nitrates by conversion to methyl nitrite and extraction with chloroform or carbon tetrachloride.[204] From coloured solutions and soils, traces of nitrite are extracted as *iso*amyl nitrite. The extract is converted to methyl nitrite with methyl alcohol, then treated with sulphanilic acid and examined colorimetrically.[205] In extremely dilute solutions, the time required for the formation of the starch-iodine colour when the nitrite is treated with potassium iodide at a constant temperature is a measure of the 'supersaturation tension', which, in turn, is dependent on the concentration of nitrite.[206] Indirect colorimetry for nitrites is based on the reaction: $HNO_2 + CS(NH_2)_2 \rightarrow N_2 + HCNS + 2H_2O$. Some boric acid and a calculated excess of ferric salt are added and the light transmitted through a green filter to a Pulfrich photometer is determined.[207] Another indirect method is the reaction between mercuric thiocyanate with nitrite to form mercuric nitrite and thiocyanate ion which gives a reddish orange colour with ferric alum; the colour is measured with a spectrophotometer at 460 mμ.[208] For nitrites in milk and milk products, a suitable colorimetric method has been described.[209–211]

Other methods. When the sample solution is treated with barium chloride and then with sulphamic acid, barium sulphate is precipitated if nitrites are present. The barium sulphate is estimated gravimetrically. If present in only minute amounts, the turbidity due to the barium sulphate is determined in a nephelometer.[212] *p*-Nitraniline can be diazotized with nitrite and coupled with α-naphthol to give an orange red precipitate quantitatively corresponding to the nitrite content; the precipitate dissolved in sodium hydroxide gives an intense blue-violet colour which may be used for a colorimetric test as well.[213] Nitrites can be precipitated as silver nitrite in alcoholic solution and the excess of silver determined by a Volhard titration.[214] Some polarographic methods are also available for the determination of nitrous acid or nitrites.[87,215] An indirect polarographic method for nitrite depends on the catalytic effect of molybdate.[216] The length of the induction period during the nitration of dimethylaniline under controlled conditions is, as indicated by turbidity, dependent on the concentration of nitrous acid.[217] Modifications of these or other methods on the estimation of nitrites under a variety of conditions are given in several other papers.[218–230]

'MIXED ACID', AND MIXTURES OF NITRATES AND NITRITES

'Mixed acid' from nitration plants may contain sulphuric and sulphonic acids, organic acids, nitrous acid and nitric acid. The total acid is easily determined by titration against standard alkali, nitrous acid by titration against potassium permanganate, and total nitrogen acids by means of a nitrometer, or by reduction to nitric oxide or ammonia, or by direct titration with ferrous sulphate or by the nitron method. To estimate nitrous acid alone, the sample is added to carbonate-free potassium citrate followed by a concentrated solution of potassium ferrocyanide; the

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volume of nitric oxide evolved is a measure of the nitrous acid present.[231] Ferrous chloride sets free nitric oxide from both nitrous acid and nitric acid, and the total can thus be determined in a nitrometer.[232] Analysis of total nitrogen acids can also be carried out by reduction to ammonia with Devarda's alloy and distillation and thence estimation of the ammonia.[233] Nitrous acid in presence of nitric acid, sulphuric acid, and sulphites is best determined by the colorimetric method with *m*-phenylenediamine.[234,235] Nitrites are determined colorimetrically with sulphanilic acid and α-naphthylamine reagent; after eliminating nitrite with urea, nitrates can be estimated by the phenoldisulphonic acid method.[236] With resorcinol, nitrites as well as nitrosyl chloride produce the pink resorufin; small amounts of nitrates do not interfere. Nitrate can, however, be determined if it is transformed to nitrosyl chloride by heating with sulphuric acid and hydrochloric acid.[237,238] General modifications of the method to suit the specific needs of the systems have been described in two other papers.[239,240]

A method of determining total nitrogen in a mixture of nitrate and nitrite as in fertilizers depends on the distillation of the neutral salt with copper–magnesium alloy in the presence of magnesium chloride and collecting the ammoniacal distillate in standard acid; the presence of free alkali nullifies the reducing power of the alloy.[241,242] The Devarda method works equally well even on the microscale.[243] Other good reducing agents are iron and copper–zinc alloy.[244,245] Milligan has detailed an important procedure for the quantitative determination of the reduction products of free nitric acid solutions, namely, nitrogen peroxide, nitric oxide, nitrous oxide, nitrous acid, hydroxylamine, hydrazine, and ammonia.[246] Some general work, with comments and reviews on the qualitative and quantitative analysis of nitrous acid, nitric acid and their salts has been given in several other papers.[247–315]

NITRO-COMPOUNDS AND EXPLOSIVES

Explosives such as gun cotton, nitroglycerin, T.N.T., smokeless powder and cordite, nitric acid esters such as nitro-starch, nitrocellulose, nitroglycol and ethyl nitrate, as well as the nitro-aromatic compounds form a class of compounds which can be estimated according to the methods available for nitrites and nitrates. After suitable modifications, the Dumas and the Kjeldahl method can be adopted for the determination of nitrogen in organic nitro-compounds.[316–319] For di- and tri-nitronaphthalenes, reduction by phosphonium iodide followed by a Kjeldahl procedure is found to be accurate and much superior to titration with titanous chloride.[320] In the Devarda procedure, the nitro-compound is warmed with potassium hydroxide and occasionally some hydrogen peroxide before it is reduced with the Devarda alloy[321]; the evolved ammonia is estimated by any of the usual methods. Experiments[322–332] on potassium nitrate and nitrocellulose show the method to have a coefficient of variation of about $\pm 0{\cdot}3\%$.[328–329] Nitric nitrogen in celluloid, guncotton, T.N.T., or other nitro-compounds has been determined by a nitrometric method. Camphor and phenylamines vitiate this determination.[333–336] Nitro-compounds are reduced to primary amines by boiling with stannous chloride and hydrochloric acid; the excess of stannous chloride can be estimated by titration with iodine.[337] Reduction by titanous chloride gives good results with metallic nitrates and many nitro-organic compounds.[338] On heating the sample with acetic acid and ferrous chloride, an equivalent amount of ferric ions is formed and can be titrated with titanous chloride.[339] Nitrocellulose and nitroguanidine both nitrate salicylic acid in sulphuric acid solution; the nitrosalicylic acid can subsequently be reduced with titanous chloride and the method employed for their estimation.[340–342] *cyclo*Trimethylenetrinitroamine is oxidized to nitrosulphuric acid, $SO_2(OH)NO_2$, which can be estimated by titration against potassium permanganate.[343] When nitro-compounds are fused with sodium or potassium hydroxide in an iron tube with aluminium, zinc, sugar, or starch, ammonia is evolved which can be absorbed in sulphuric acid and estimated.[344] The ter Meulen method of hydrogenation gives satisfactory results when larger amounts of active nickel catalyst are used and the substance to be reduced is applied to the catalyst surface so that it is more finely divided on the surface.[345] Since acidified organic nitrites liberate iodine from hydrogen iodide, they can be estimated iodimetrically.[346] When nitroglycerol is evaporated with a concentrated solution of potassium hydroxide, two molecules of potassium nitrite and one molecule of potassium nitrate are obtained; these can be estimated by the usual methods.[347] Marqueyrol has given a collection of various notes on the determination of nitrogen by methods which have long been studied in the French Powder Service.[348] Verschragen has made a comparison of the various methods used in the European countries for the determination of the nitrogen content of nitrocellulose.[349] Some general remarks on the analysis of nitro-compounds are to be found in several other papers.[350–358]

HYPONITRITES

Hyponitrite is estimated volumetrically with potassium thiocyanate. If in presence of other oxyacids, both nitrite and hyponitrite can be precipitated as silver salts, and the nitrate determined by difference.[359]

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Determination of Nitrogen in Fertilizers

The common constituents of nitrogenous fertilizers are the nitrates, ammonium compounds, urea, cyanamide and oil cakes or other organic fertilizers. The analysis of the individual components in the presence of others is indicated below.

ANALYSIS AS AMMONIA

Analysis of ammoniacal, nitric and organic nitrogen in mixed fertilizers consists of three determinations in the form of ammonia: (*a*) free ammonia in an aqueous extract or in a distillate obtained in the presence of magnesium or sodium hydroxide; (*b*) nitrates after reduction with Devarda's alloy, iron–zinc alloy or some other suitable agents; and (*c*) residual nitrogen after a Kjeldahl treatment of the insoluble residue with suitable catalysts.

Ammonia is estimated by any of the usual methods such as the formol titration or hypobromite method.[1–8] In complex fertilizers with a base of calcium cyanamide and ammonium salts, treatment with sodium carbonate liberates ammonia first from the ammonium salt and then from cyanamide.[9] The formol titration can be employed for the estimation of ammoniacal components; from certain types of compounds, ammonia is liberated by distillation with magnesium oxide or by aeration in the presence of sodium hydroxide.[10–14] Ammoniacal nitrogen can also be determined by a visual conductivity titration; the method is especially applicable to ammonium sulphate and phosphate fertilizers.[15] In a comparative study of the Devarda method, the direct formol titration method and the distillation over magnesium oxide or sodium hydroxide, all four methods show the feasibility of approaching the theoretical amount of nitrogen in ammonium nitrate; the formol titration method seems to be the simplest. For nitrate–chloride mixtures, some modifications are necessary, one of the modifications being the use of reduced iron.[16–21] The Kjeldahl method has been thoroughly reviewed by some authors.[22,23] Alkaline permanganate can be used to oxidize the available nitrogen in organic manures to ammonia but it has been found to be defective unless stringent procedures are followed.[24–32] By heating the sample in a copper tube with solid sodium hydroxide and sodium acetate, ammonia is evolved, and this can be absorbed in an acid and estimated by a suitable method.[33]

ANALYSIS OF CYANAMIDE

A complete analysis of cyanamide fertilizers involves the determinations of (*a*) the total nitrogen by the Kjeldahl method, (*b*) ammonia by formol titration, (*c*) urea by the xanthhydrol method, and (*d*) dicyanodiamidine by means of its insoluble nickel salt.[34–40] The total nitrogen in calcium cyanamide has been determined by heating the sample to 700°C. in a current of hydrogen chloride when calcium chloride, carbon tetrachloride and ammonia are formed quantitatively; the ammonia is estimated by one of the usual methods.[41] In a modification of the Kjeldahl procedure for total nitrogen, the acid after digestion is neutralized and the ammonium salt determined by a formol titration or a bromometric method.[42–44] Cyanamide, $CN \cdot NH_2$, is determined by precipitation with silver acetate in 2% acetic acid; dicyanodiamide is not precipitated in this process.[45] When calcium cyanamide (or compounds like thiourea, uric acid and caffeine) is heated with concentrated sodium hydroxide under pressure in an autoclave, ammonia is evolved. This is absorbed in standard acid and analysed by any of the usual methods; the relative error is ±1%, and the method is suitable for control work.[46] Analysis of the urea components of cyanamide fertilizers has been reviewed by Cochet.[47] Some other analytical methods for cyanamide, either alone or in admixture with nitrate or phosphate fertilizers, have also been mentioned in the literature.[48–52]

ANALYSIS OF OTHER FERTILIZER MIXTURES

The method of determining nitrogen in liquid manure by measuring the specific gravity has been found to be incorrect.[53] Detection and determination of nitrate, cyanamide, ammonium salts and urea in mixed fertilizers has been the subject of several reviews.[54–58] For total nitrogen or for the nitrogen in the insoluble organic residue, a Kjeldahl digestion with phenolsulphonic acid, sulphuric acid, zinc powder, sodium sulphate and mercury is necessary; nitrate plus ammoniacal nitrogen is determined by distillation with powdered zinc and ferrous sulphate; ammoniacal nitrogen by distillation with magnesium oxide; and if cyanamide or urea is present, the Kjeldahl digestion should be performed in the presence of ferrous sulphate.[59] There are similar procedures for separately determining total nitrogen, nitrate, ammonium salts, urea and derivatives of cyanamide.[60,61] Some general remarks on the analysis of nitrogenous fertilizers are also to be found in several other papers.[62–74]

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Determination of Nitrogen in Natural Products

Here are grouped the analytical methods for a large number of natural materials—air, mist, fog, snow, water, sewage, soil, coal and coal products, fuel oils, leather and hide, biological materials and ecological products. The analysis of these materials has been mentioned in some of the previous sub-sections. The various methods for each are co-ordinated in the following paragraphs.

AIR AND ATMOSPHERE

Air pollution may be a serious problem in an industrial vicinity, and the sampling of air and its analysis for oxides of nitrogen, ammonia and hydrogen cyanide are of great importance.[1,2] In evaluating atmospheric contamination, an electrostatic precipitator, cascade impactor, thermal precipitator, Venturi scrubber and mechanical filters can be used to collect samples for optical or colorimetric methods of analysis.[3,4] Samples of soil air can be withdrawn by means of a hypodermic syringe.[5] For minerals, samples have to be crushed, ground and degassed in a special apparatus.[6]

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Simple absorption by passing the air through sulphuric acid gives the amount of ammonia.[7] Nitrogen dioxide is absorbed in acidified permanganate and nitric oxide in ferrous sulphate or potassium permanganate.[8] Nitrogen in air is determined by passing an electric spark through a mixture with oxygen until no further reaction takes place. The mixture is then passed through potassium hydroxide solution and the amount of nitrogen computed.[9] Carbonaceous gases are detonated and absorbed in suitable solvents leaving behind the nitrogen for separate analysis.[10] A physical method for determining nitrogen, ammonia and other gases is afforded by thermal conductivity measurement.[11] The depth of colour produced when a drop of Nessler reagent is exposed to air, such as that of stables, is a measure of the ammonia concentration.[12] In respiratory research direct reading nitrogen analysers are very often used.[13,14] To determine ammonia in mine gas, it is passed through dilute hydrochloric acid which is later titrated with Congo Red indicator; cyanides are determined by alkaline ferrous sulphate and thiocyanates by very dilute ferric chloride.[15] The Dumas method gives quantitative results for nitrogen in natural gases.[16] Other references concern the analysis of air and coal gas.[17–19]

WATER AND SEWAGE

The amount of nitric acid and nitrous nitrogen as well as free, saline and albuminoid ammonia in water and sewage has been determined by a variety of methods.[20–26] The ammonia in water and sewage is determined by a Nessler method in the presence of sodium potassium tartrate which prevents interference from some of the metal ions.[27–31] The colorimetric method for ammonia is not always directly applicable for sewage, and the ammonia has to be recovered by a distillation or aeration method.[32,33] The blue colour developed with phenol and sodium hypochlorite is a measure of ammonia in sea water.[34,35] For the analysis of ammoniacal and industrial waters the formol titration is applicable.[36,37] Ammonia can be distilled over magnesia and estimated titrimetrically. In this case, urea is also decomposed and its products distil.[38,39] In the presence of nitrates and nitrites, free and saline ammonia is first distilled, the nitrate is then reduced by zinc and acids, and finally the residue subjected to a Kjeldahl treatment. Total nitrogen is also determined by a Kjeldahl procedure.[40–43] If a strong alkali is used in liberating the free ammonia from ammonium salts, some hydrolysis of organic nitrogen compounds might take place; it is therefore safer to use a buffer solution composed of potassium dihydrogen phosphate and potassium monohydrogen phosphate, or the latter substance with sodium hydroxide.[44,45] For quantitative distillation of all the saline ammonia, it is necessary to add carbonate of sodium, magnesium or calcium.[46] Empyreumatic products interfere with the determination of ammonia by means of Nessler solution unless the ammonia has been distilled under vacuum.[47] Ammonia can be determined by the Conway microdiffusion technique. The method is applicable to the analysis of nitrate or nitrite by reduction with Devarda's alloy or Raney nickel in presence of ethylenediaminetetra-acetic acid.[48,49] A simple process for ammonia in sea water is oxidation with sodium hypobromite and estimation of the excess hypobromite with Bordeaux dye.[50] Nitrous acid, nitric acid, or their anhydrides in micro amounts have been determined by a colorimetric procedure.[28,51,52] Lewin has reviewed the volumetric, colorimetric and gasometric procedures for nitrites and nitrates: the *m*-xylenol method for nitrate and Griess–Ilosvay method for nitrite are regarded as best standards.[53] Nitrates and nitrites could be reduced by Devarda's alloy and the ammonia estimated titrimetrically or colorimetrically.[54] Only negligible hydrolysis of organic nitrogen occurs during the treatment with sodium hydroxide and Devarda's alloy.[55] Protein or albuminoid nitrogen is determined by digestion with sulphuric acid and potassium persulphate followed by treatment with Nessler's reagent; if digestion is carried out with alkaline permanganate, distillation is necessary before colour development.[56–59] Total nitrogen is determined by means of a Kjeldahl digestion of the residue left on evaporating a sample of water; sulphuric acid or potassium acid iodate is used in the digestion.[60,61]

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To remove fog and mist for analysis, the mixture may be passed through a porous membrane or treated in a Cottrell precipitator.[62]

In a general analysis of sewage, ammonia is determined by using Nessler's reagent in presence of Rochelle salt, nitrite by a diazotization method, nitrate by phenolsulphonic acid, thiocyanate by its reaction with ferric chloride, and cyanide by Weehuizen's method.[63,64] The analytical procedure for water has been reviewed by Fujiwara,[65] and many other authors have discussed the analysis of water and sewage in a general way.[66–112]

SOIL

Proper sampling of soils is a prerequisite for the successful evaluation of its nitrate, nitrite and ammonia content.[113,114] A 25% sodium perchlorate solution buffered at pH 4·8 is used for the extraction of nitrate nitrogen and ammonia from soils; potassium sulphate, potassium chloride, potassium aluminium sulphate and a mixture of sulphuric acid and sodium borate are also used for extracting the inorganic nitrogen compounds in soils.[115–117] An electro-ultrafiltration of soils can be applied to the determination of bases, ammonia and nitrates.[118] Analyses of wet field samples of soils give a truer picture of the available ammoniacal and nitrate nitrogen than do analyses of air-dried or oven-dried samples.[119,120]

Digestion of the samples with alkaline permanganate and estimation of the ammonia after distillation gives results comparable with the mineralized nitrogen released after prolonged incubation.[121] Total nitrogen is obtained by a Kjeldahl procedure. The use of selenium in presence of perchloric acid reduces the digestion time considerably in soil and food analysis.[122] A rapid method for total nitrogen is to digest the soil extract with monochloroacetic acid, sodium chlorate and fuming sulphuric acid; the digest is treated with phenolsulphonic acid and the colour compared with standards.[123] During the normal Kjeldahl procedure for total nitrogen, the protective action of silica has to be overcome by suitable modifications.[124–134] A chlorate method has been stated to be quicker than the Kjeldahl procedure.[135–137] Other suggestions are the use of chromic–sulphuric acid mixture or alkaline permanganate for digestion.[138–142] The residue of a wet combustion method can easily be used for total nitrogen estimation.[143,144] A vacuum combustion or a modified Dumas method has also been employed for total nitrogen.[145–147] Another suggestion is a biochemical process based on catalase activity.[148,149] Nitrates and nitrites are determined by colorimetric or reduction methods.[150] Reduction with iron powder in sulphuric acid is as suitable a method as reduction with Devarda alloy in alkali.[151,152] Ammonia is recovered by distillation or aeration of a sample made alkaline with sodium hydroxide, sodium carbonate or magnesia, very often in the presence of sodium chloride. In many cases, the soil is first extracted with alkali metal chloride solutions and then treated with alkali for the recovery of ammonia. This method can be coupled with micro-diffusion colorimetry for ammonia. Amino-nitrogen is determined by extracting the soil with hydrochloric acid or acetic acid–sodium acetate buffer and finally using the Kjeldahl method on the residue. Dilute hydrochloric acid is also a solvent for the extraction of available nutrient elements; in the extract, nitrate can be determined by diphenylamine sulphate. Ammonia is best estimated colorimetrically, for example, by Nessler reagent.[153–167] Nitrites can be determined by a variety of colorimetric methods.[168] Titrimetrically, nitrites are determined by treating with excess of hydroxylamine and estimating the excess of hydroxylamine.[169] When allowance is made for nitrite, reduction methods using zinc and ferrous sulphate, or alkali and Devarda's alloy, or the colorimetric method with phenolsulphonic acid, are satisfactory for nitrates. Nitrate plus nitrite is determined by reaction with brucine, nitrites alone by Griess reagent or dimethylaniline, and ammonia by Nessler reagent.[170–175] There are several reviews on the analysis of soil for its mineral nitrogen, nitrogen that can be mineralized, and inorganic nitrogen.[176–178] General remarks on soil analysis are also found in a large number of papers.[179–248]

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COAL, COAL PRODUCTS AND FUEL OILS

The Kjeldahl and the Dumas methods are those commonly recommended for the analysis of total nitrogen in fuels. The Kjeldahl results are somewhat low and the Dumas results are a little too high.[249] The low results in the Kjeldahl method are probably due to loss of nitrogen as the gaseous element during the digestion.[250–260] Satisfactory modifications are: (*a*) provision for measuring the nitrogen that comes off as elementary gas and not as ammonia[261]; (*b*) oxidation of coal with concentrated sulphuric acid and manganese dioxide, potassium permanganate or in the presence of suitable catalysts[262–268]; (*c*) controlling the rate of heating and the use of selenium catalyst[269,270]; (*d*) use of vanadium pentoxide with or without selenium as a catalyst in the second stage or after boiling[271,272]; and (*e*) grinding the coke to −240 mesh and using a high concentration of potassium sulphate.[273]

In the Dumas method applied to fuels, unabsorbable gases like oxygen, carbon monoxide and methane are also present in the gaseous products even if the combustion is carefully carried out. Satisfactory modifications are: (*a*) the use of potassium chlorate with or without manganese dioxide in the combustion tube for the generation of oxygen to aid combustion[274,275]; (*b*) treatment of the gases in the nitrometer with alkaline pyrogallol and ammoniacal cuprous chloride in Hempel pipettes so as to eliminate the interfering gases[261]; (*e*) complete combustion of the gases with the aid of oxygen produced by electrolysis or by other methods[276–278]; (*d*) catalytic explosion or combustion of all extraneous hydrocarbons and their absorption in suitable reagents[279–282]; (*e*) ensuring complete combustion of methane and carbon monoxide by covering the coal sample with a layer of cupric oxide and carrying out the combustion in electrolytic oxygen[283]; (*f*) generation of carbon dioxide and oxygen in the same flask by adding sodium carbonate and hydrogen peroxide respectively to the flask containing sulphuric acid and potassium dichromate[284]; (*g*) mixing coke with lead chromate at 850°C. in a current of carbon dioxide[285]; (*h*) heating the coal mixed with tellurium oxide and passing the escaping gases repeatedly over glowing cupric oxide[286]; and (*i*) using a special cupric oxide–ferric oxide catalyst.[287]

For the determination of nitrogen in coal oxidation products, a zinc amalgan reduction method has been developed; after reduction, the solution is titrated with standard sodium nitrite solution using potassium iodide–starch indicator.[288] The determination of nitrogen by catalytic hydrogenation fails with coal unless suitably modified.[289] But the element is completely converted to sodium cyanide when the coal is fused with sodium carbonate; the cake evolves ammonia when treated with water, and the ammonia can be estimated by any of the usual methods.[290]

A recent method is the combustion of coke or coal in steam in the presence of catalysts such as vanadium pentoxide and molybdic acid: ammonia is produced quantitatively. This method is more accurate than the Kjeldahl procedure and agrees very closely with the improved Dumas method.[291–294] Another method involves heating the sample with magnesium powder at 560–650°C. to obtain magnesium nitride; decomposition of this gives ammonia which can be estimated by a suitable method.[295]

Determination of ammonia in ammoniacal liquors involves the use of the Hempel explosion and absorption pipettes or allied methods.[296–298] To determine pyridine in gas liquor distillates, the ammonia is destroyed by sodium hypobromite and the pyridine distilled over to standard hydrochloric acid for estimation.[299]

For the analysis of nitrogen in petroleum oils, the Kjeldahl method has to be suitably modified, particularly with regard to the addition of glucose and catalysts.[300–303] Use of the phenol–hypochlorite colorimetric procedure for ammonia permits detection of 1 p.p.m. of total nitrogen in a 5 g. sample.[304,305] The Dumas and the ter Meulen catalytic hydrogenation method are sometimes applied.[306] Probably the best method is the hydrogenation method, consisting of the decomposition of the sample in an atmosphere of hydrogen, conversion of nitrogen to ammonia by passing the decomposition products over nickel–magnesium catalyst, absorption of ammonia from the gas in boric acid and titration with standard hydrochloric acid.[307] The ratio of basic to total nitrogen is found by titration against perchloric acid.[308,309] Nitrogen compounds in petroleum distillates, such as pyridine, quinoline and pyrrole derivatives, are absorbed on a small column of silica gel and the nitrogen is determined by subjecting the silica gel to the Kjeldahl procedure.[310] These compounds can also be determined by suitable colorimetric methods.[311] Ammonia, for example, is determined by heating a sample with sulphuric acid, adding alkali and estimating the evolved ammonia colorimetrically with Nessler reagent.[312] Many general remarks on the analysis of nitrogen in coal, coke, shale oils or other fuels are found in several papers.[313–342]

PLANT AND ANIMAL PRODUCTS

This sub-section covers the analyses of the following materials: blood, biological fluids, fæces, urine, seeds, plant tissues, pulp and paper, cotton, linen, wort, latex, yeast, sugar products, oils, fats, milk and milk products, and egg. From blood, urine, soaps, oil preparations, opiums, egg albumin and fæces, ammonia is usually aerated from alkaline solutions containing magnesia, sodium or calcium hydroxide, borax or a phosphate buffer; ammonia can also be steam-distilled or vacuum distilled. The recovered ammonia is estimated by a titration of an acid–base or hypobromite type, or by a colorimetric procedure using Nessler reagent or the phenol–hypochlorite reagent. Interference from phosphates can be prevented by removing them as a precipitate with lead acetate or lead carbonate. Ammonia in certain cases can be precipitated as magnesium ammonium phosphate and then estimated by a suitable procedure. For blood, alcohol is a good agent for removing protein. Milk proteins are precipitated with magnesium sulphate, mercuric nitrate, uranyl acetate, zinc hydroxide or sodium tungstate.[343–381] Generally, physiological fluids containing nitrogen compounds of plant or animal origin evolve ammonia when heated with alkaline potassium permanganate or periodate.[382–385] In some cases, a simple digestion suffices to liberate all the ammonia from proteins.[386] Ammonia-forming nitrogen in blood is removed by dialysis against a buffer solution.[387] Ammonia is separated from urea in urine by means of steam-distillation in alcohol, by cation-exchange resins or by absorbing the ammonia in a permutit.[388–393] The permutit absorption method has also been employed for the determination of ammonia in milk and plant juices.[394,395] Ammonia in silage is separated by means of paper chromatographic methods using $2+1$ (v/v) butanol–6N-hydrochloric acid as solvent.[396,397] After separation of ammonia, a simple procedure for its estimation is the formol titration.[398–400]

The difficulties of foaming and excessive time of digestion during the Kjeldahl analysis of plant or animal materials are overcome by adding hydrogen peroxide or perchloric acid. The standard Kjeldahl procedure has to be modified to suit each kind of sample. Precipitation with lead acetate or trichloroacetic acid separates the proteins from the non-proteins, and a Kjeldahl digestion of both the precipitate and the filtrate enables the determination of protein as well as non-protein nitrogen to be made.[401–433] Compared with the Kjeldahl method, higher values are always obtained for the Dumas procedure.[434] Ammonia can be separated from amino-acids in urine by means of precipitation with Na_2HPO_4 and basic magnesium carbonate.[435] A quick method for the determination of nitrogen in starch is digestion with sulphuric acid and hydrogen peroxide, and estimation of ammonia with hypobromite or Nessler reagent.[436] Amino-nitrogen in blood, urine, cream and butter is determined by the Van Slyke method,[437,438] and that in sugar products colorimetrically.[439] Trimethylamine and ammonia present in foodstuffs are distilled from magnesia and estimated by acid titration.[440] Similarly, ammonia and nicotine present in tobacco are distilled over magnesia and estimated together by acid titration; ammonia alone is determined by formol titration or by its reaction with nitrous acid.[441–444] The other forms of nitrogen in tobacco have to be analysed by different methods.[445–455] In fish extracts, ammonia is removed as an insoluble mercuric complex by means of an

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alkaline suspension of mercuric oxide so that the amines can then be estimated.[456] Ammonia in bisulphite pulp-cooking liquors has been determined by the use of bleaching powder.[457]

The total nitrate and nitrite in plant tissues and molasses is determined by reducing the aqueous extract with Devarda's alloy in alkali and estimating the ammonia evolved.[458–460] The manometric procedure has been extended to the analysis of nitrites and nitrates.[461] In another method, the protein is removed by mercuric chloride, and the nitrate determined by the blue colour produced on the addition of diphenylbenzidine and sodium chloride.[462, 463] To determine nitrites in urea, salipyrine in sodium acetate has been used as a colorimetric reagent.[464] Various other methods for nitrite and nitrate have been given by Hänni.[465]

A complete analysis of malt wort or plant extracts involves the determination of total nitrogen, ammonia, and amino-, amide- and peptide nitrogen.[466, 467] Crystal formation after treatment with 2:4-dinitronaphthol constitutes a principal amine test.[468] Urea in urine and in the extracts of feathers and down is determined by urease decomposition; to determine urea and ammonium salt, the solution is hydrolysed with alcoholic alkali and the total ammonia determined by a suitable method.[469–472] Improved spectrophotometric methods have been described for the determination of ammonia, uric acid, creatinine and allantoin in biological fluids.[473] An electrodialysis method is applicable to the determination of total base in serum, blood cells, urine, tissues and other biological fluids.[474] In plant tissues, nitrogen in the form of ammonia, amino-protein, amide, nitrate and alkaloid is determined by a chlorate oxidation.[475] Oxidation with sulphur trioxide and sodium perchlorate in the presence of chloroacetic acid converts all forms of nitrogen to nitric acid, which can be determined colorimetrically.[476] Detailed directions for determining total nitrogen, insoluble and soluble protein nitrogen, total soluble nitrogen, ammonia, α-amino nitrogen, amide, urea and nitrate in crude proteins have been given; the method is based on the various aspects discussed above.[477] By another standardized procedure, plant extracts can be analysed for their ammonia, amide, nitrite and nitrate.[478] General references to the analysis of the various forms of nitrogen in foodstuffs, urine, blood or other biological fluids, plant tissues and medicines are to be found in many papers.[479–616]

MEAT PRODUCTS

The filtered extract from the salted meats is treated with colloidal hydrated ferric oxide to precipitate proteins and colouring matter and filtered again. To estimate nitrite, the filtrate is treated with *m*-phenylenediamine in acetic acid–sodium acetate buffer; other suitable reagents are sulphanilic acid and naphthylamine or phenolsulphonic acid. The coloration produced is compared with standards made from sodium nitrite.[617–620] Nitrites in deproteinated meat extracts are estimated by an iodimetric method.[621] While the tests using diphenylamine–brucine or sulphamic acid are suitable for nitrite, gasometry with the liberated nitric oxide is preferred in the case of nitrates.[622] Colorimetrically, nitrates are analysed by making use of the product of nitration of 4-hydroxy-1:3-dimethylbenzene.[623] A polarographic method has been developed for nitrates, nitrites and for the approximate determination of total protein.[624] Ammonia in the meat can be extracted with carbon tetrachloride and the extracted ammonia distilled over to standard acid for titrimetric estimation; ammonia can also be estimated by other methods.[625–627] Some general references for the analysis of salted meat are also to be found.[628–632]

LEATHER, HIDE AND PELT

There are a few references on the general analysis of tannery soap, bate and lime liquors for their total nitrogen, proteins, and ammoniacal and amino nitrogen, although some mention has been made of these in the previous sub-sections.[633–635] Free ammonia in used bate liquors is determined by titration with standard acid using hæmatin indicator.[635] Proteins can be hydrolysed with hot sodium hydroxide and the liberated ammonia estimated by a suitable method.[636] To determine the total nitrogen in leather by the Kjeldahl method, addition of perchloric acid is found to be beneficial; mercuric iodide used as a catalyst saves much time in the digestion. The ammonia is distilled over to acid and estimated.[637–640] Similar or other general methods for the estimation of nitrogen in leather have also been described.[641–651]

GENERAL

Several other remarks of a general nature have been made on the estimation of nitrogen in natural products such as water, soils, sewage, urine, biological and plant fluids, and many others. These refer to the multifarious forms of the nitrogen compounds and more complex organic compounds occurring therein, and their determination employs essentially the same procedures as those described in the preceding sections or are more relevant to a work on detailed organic analysis.[652–683]

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